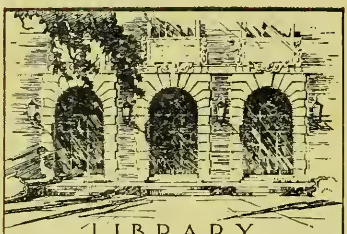

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Contribution from the North Carolina Experiment Station.[1]

FACTORS OF AVAILABILITY OF PLANT FOOD.

BY G. S. FRAPS.

Plant food which can be removed from the soil by a crop is said to be available. When fertilization with phosphoric acid produces a decided increase in crop, the soil is said to be deficient in available phosphoric acid. Deficiency in available potash or nitrogen is judged in the same way. A rich soil contains abundant supplies of available plant food; a poor soil may be deficient in one or more essential elements, though other influences may cause a soil which contains an abundance of available plant food to yield poor crops. The term "available" refers to the plant food which can be taken up from the soil by a crop and has especial reference to the effect of phosphoric acid, potash, or nitrogen in increasing yields.

Deficiency in available plant food is usually judged from plot or pot tests, with the use of different fertilizers. Field experiments must be carried out at least two years, and even then the conclusions are not always reliable.[2]

For several decades chemists have been endeavoring to devise a method for the determination of available plant food in soils. The search has been for solvents which would always dissolve less phosphoric acid from soils deficient in this element than from fertile soils, and less potash from those deficient in potash than from fertile soils. While valuable results have been obtained in this work, we have as yet no method which can be relied upon to show whether a soil requires fertilization with potash or phosphoric acid. Solvents are known which furnish valuable data with certain kinds of soils, but fail with others. It is possible that this is in part due to the fact, as Hartwell[1] has pointed out, that the soils worked on may not be deficient in what they are supposed to be. It is also possibly due to lack of consideration of other factors than solubility.

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[1] This work was performed in this laboratory with the permission of Prof. W. A. Withers, Chemist.

[2] See Hartwell: Proc. Assoc. Offic. Agr. Chem., 1900, p. 73.

Very often there is no relation between the plant food dissolved by a given method and the fertility of different soils. Under such circumstances, the rule has been to decide that the method of determining available plant food is at fault. The authors of a recent article, however, who assumed that the plant food dissolved by water from soils was a measure of the available food, have gone so far as to conclude that, since there is no relation between the water-soluble plant food in a soil and its fertility, the latter does not depend on the amount of available plant food in the soil, but on unknown physical factors.

Factors of Availability.

Considering availability as referring to the plant food taken from the soil by crops, under favorable conditions of moisture, temperature, etc., it is well to consider whether other factors than the solubility of the plant food are not involved. It is a very well-known fact that in the case of nitrogen the amount of nitrates is no measure of the available nitrogen, since the presence of 2 or 20 parts of nitrates per million is no indication how much or how little nitrates will be produced during the growing season of the crop. Further, complex silicates are known to decompose in the soil, with the production of more soluble compounds of potash. This process may take place so slowly as to be inappreciable from year to year, but in long periods of time weathering is of importance. Four factors, or rather groups of factors, may be considered as influencing to a greater or less extent the availability of any given element of plant food. These are as follows:

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[1] See Hartwell: Proc. Assoc. Offic. Agr. Chem., 1900, p. 73.

1. The quantity of the element present at the beginning of the growing season in forms of combination which can be directly absorbed by plants. This may be called *chemical availability.*

2. The condition of the soil particles. Compounds chemically available may be protected, or enclosed, so as not to be exposed to the action of soil moisture or plant roots. This may be called *physical availability.*

3. The amount of the element transformed during the growing season into forms of combination which can be directly absorbed by the plant. Processes of weathering slowly transform the less soluble into more soluble compounds. This factor is certainly of importance in the case of nitrogen ; its importance in the case of potash and phosphoric acid remains to be determined. This factor may be called *weathering availability.*

4. The nature of the plant. Plants differ in their capacity for absorbing plant food. It has been disputed whether plants do not take up all their food from soil solutions, but however this may be, plants differ in their capacity to absorb food. We will call this factor *physiological availability.*

Thus four factors have been included under the term availability. Chemists have chiefly directed their attention to the first, namely, the chemical availability, more particularly with reference to the solubility of the plant food. The other factors cannot be disregarded until their non-importance has been established. It remains to be demonstrated whether the lack of success in finding a solvent for estimating available plant food is due to incomplete knowledge in regard to the soils worked on, or to neglect of those other factors, or both.

Chemical Availability.

The solvent power of plants has not yet been worked out. It is certain that plant roots can take up plant food dissolved in the soil water, but to what extent they can act upon undissolved food is not known. The intimate contact of soil particles and roots, the presence of acid juices in the roots, and certain experiments, are in favor of the view that plants can take up food from other than the soil solution.

Cell walls of plant roots are semipermeable membranes, penetrable by K, PO_4 and other ions. On one side of the cell wall is an acid solution, which must be dissociated to a certain extent with the production of hydrogen ions; on the other side, the soil particles. According to the laws of diffusion, the hydrogen ions should penetrate the cell walls and act upon the soil particles, bringing insoluble bodies into solution.

Dietrich[1] grew plants in pots of new red sandstone and basalt, which was also allowed to weather in pots kept free from vegetation. At the end of the experiment the mineral matter in the plant was added to that dissolved from the soil by 1 per cent nitric acid, and the mineral matter made soluble by weathering was subtracted. The difference represents the solvent effect of the plants:

Solvent Action of Plants.

Plant.	Total mineral matter. Sandstone. Gram.	 Basalt. Gram.
Three lupine plants	0.6080	0.7492
Three pea plants	0.4804	0.7132
Eight wheat plants	0.0272	0.1958
Eight rye plants	0.0137	0.1316

This is certainly evidence that plants can take up mineral matter other than that in the soil solution. The figures also exhibit a striking difference in the solvent powers of the plants.

Physiological Availability.

A difference in the power of plants to take food from the soil has been recognized for some time. Kossovich[2] divides plants into five groups, according to their ability to assimilate the phosphoric acid of phosphates. 1. Plants of high capacity—mustard, buckwheat, hemp, winter rye. 2. Plants of medium capacity—peas, barley, summer rye, beets. 3. Plants of low capacity—potatoes, vetch, oats. 4. Plants almost devoid of capacity—millet, flax, clover.

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[1] Jsb. Agr. Chem., 1863, p. 1.

[2] Expt. Sta. Rec., 13, 265.

Wagner[1] states that under the most favorable conditions the following percentages of the nitrates added to a soil are recovered in the crop :

90 per cent by potatoes, carrots, turnips ;
75 per cent by oats and flax ;
60 per cent by barley, summer wheat, summer rye ;
55 per cent by rape, mustard.

Without going into the cause of these differences, it is clear that differences exist, and that a soil may contain sufficient available plant food for one crop, and yet be deficient in one or more elements for another.

Weathering Availability.

This is the term applied to the transformation of plant food from unavailable to chemically available forms during the growth of the crop. It is certainly of great importance in the case of nitrogen. The activity of weathering depends upon a number of sub-factors, such as the nature of the soil, the temperature, etc.

Reverse Weathering.—This term may be applied to chemical reactions in the soil which convert chemically available plant food into unavailable forms. Whether the fixing of potash salts by zeolitic silicates is not, in part, reverse weathering remains to be decided, but the transformation of soluble phosphates into aluminium and iron phosphates is very probably such a change.

EXPERIMENTAL PART.

Effect of Weathering upon Chemically Available Food.

The objects of this work were two : to ascertain if the effect of weathering upon chemically available potash and phosphoric acid could be neglected ; and second, to determine the effect on weathering of various additions to the soil, particularly organic matter.

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[1] Landw. Versuchs-Sta., 43, 127.

The plan of the experiment comprehended the use of several solvents to determine the effect of weathering. The work has, however, been confined to N/5 and N/50 nitric acid. The former solvent has been used to a considerable extent for the determination of available phosphoric acid and potash. While N/5 nitric acid cannot be asserted to be a measure of the chemically available plant food with soil, yet, since it has been used for available food, it will aid in deciding whether the factor of weathering is to be neglected. It is not believed by the author that the plant food dissolved by N/5 acid represents the chemically available plant food in the soil.

Plan of Experiment.—Three soils were selected, and from each soil a series of jars (containing 2500 grams soil) were prepared, with additions as follows :

Jars 1 and 11, nothing ;
Jars 3 and 13, calcium carbonate (25 grams) ;
Jars 5 and 25, calcium sulphate (25 grams) ;
Jar 7, starch (200 grams) ;
Jar 9, sawdust (200 grams).

Jars 1, 3, 5, 7, and 9 were kept moist by the addition of water at the beginning of the experiment and at intervals during the period (three months). Jars 11, 13, and 15 were kept dry for comparison.

At the end of the period the samples were dried and potash and phosphoric acid determined with N/5 (and potash with N/50) nitric acid according to the methods of the Association of Official Agricultural Chemists for N/5 hydrochloric acid. The determinations were not made in duplicate.

The soils are described as follows :

1786. Sandy soil from the State farm of the North Carolina Department of Agriculture, furnished through Prof. B. W. Kilgore.

1787. Cecil sandy loam from farm of A. and M. College, near Raleigh. A good soil.

1788. Durham sandy loam from College farm. Very poor.

Weathering by Moisture.

The effect of moisture alone on chemically available potash and phosphoric acid (measured with N/5 nitric acid) is presented in Table I. Potash was determined by N/5 and N/50 acid, and the figures at the head of the columns refer to this fact. The difference between the moist soil with calcium carbonate and the dry soil with calcium carbonate does not represent the action of moisture alone, since the moisture brings the calcium carbonate into action. The same may be said with regard to the calcium sulphate.

There is an average increase of chemically available potash and phosphoric acid in two soils (about 10 per cent) and a decrease in one. A difference in the behavior of the three soils is to be observed. The general effect of moisture is to increase the chemically available plant food in the soils.

Calcium carbonate seems to decrease the effect of moisture, since a less gain or a greater loss of chemically available potash and phosphoric acid takes place in its presence.

Effect of Calcium Carbonate and Calcium Sulphate.

Table II. exhibits the effect of calcium carbonate and calcium sulphate. It is seen that their presence in the dry soil affects the amount of phosphoric acid or potash dissolved by N/5 or N/50 nitric acid. Either the presence of calcium salts affects the solvent power of nitric acid of this strength, or they act upon the soil during the extraction with the solvent. In any event, a soil containing 1 per cent calcium carbonate or sulphate would give up different quantities of chemically available plant food (measured by this solvent) than the same soil without the calcium salts, and the presence of these substances would have a profound effect upon the real or apparent chemical availability of plant food in the soil.

With calcium carbonate there is an average loss of chemically available phosphoric acid with two soils, and a loss of potash in every case. The loss is greatest with soil 1787 for N/5 acid, being about 30 per cent, and about the same with soil 1788 with N/50 acid. In every case, save one, moisture

Table I.—Effect of Moisture on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786. P. Per cent.	Soil 1786. K N/5. Per cent.	Soil 1787. P. Per cent.	Soil 1787. K N/5. Per cent.	Soil 1787. K N/50. Per cent.	Soil 1788. P. Per cent.	Soil 1788. K N/5. Per cent.	Soil 1788. K N/50. Per cent.
1	Moist	.....	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
11	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)		+0.0006	—0.0007	+0.0013	—0.0007	+0.0012	—0.0010	0.0000
3	Calcium carbonate (moist)	0.0034	0.0036	0.0078	0.0074	0.0035	0.0067	0.0068	0.0048
13	Calcium carbonate (dry)	0.0041	0.0033	0.0090	0.0073	0.0055	0.0066	0.0088	0.0045
	Gain (+) or loss (—)	—0.0007	+0.0003	—0.0012	+0.0001	—0.0020	+0.0001	—0.0020	+0.0003
5	Calcium sulphate (moist)	0.0061	0.0058	0.0114	0.0095	0.0039	0.0081	0.0061	0.0058
15	Calcium sulphate (dry)	0.0045	0.0032	0.0112	0.0080	0.0056	0.0073	0.0061	0.0057
	Gain (+) or loss (—)	+0.0016	+0.0026	—0.0002	+0.0015	—0.0017	+0.0008	0.0000	+0.0001
	Aver. gain (+) or loss (—)	+0.0005	+0.0012	—0.0007	+0.0010	—0.0015	+0.0007	—0.0010	+0.0001

Table II.—Effect of Calcium Sulphate and Carbonate on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786.		Soil 1787.			Soil 1788.		
		P. Per cent.	K N/5. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.
13	Calcium carbonate (dry)	0.0041	0.0033	0.0090	0.0073	0.0055	0.0066	0.0088	0.0045
11	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)	—0.0006	—0.0002	+0.0013	—0.0025	—0.0006	+0.0003	—0.0002	—0.0027
3	Calcium carbonate (moist)	0.0034	0.0036	0.0078	0.0074	0.0035	0.0067	0.0068	0.0048
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0013	—0.0005	+0.0008	—0.0037	—0.0019	—0.0008	—0.0012	—0.0024
Aver. gain (+) or loss (—)		—0.0010	—0.0004	+0.0011	—0.0031	—0.0013	—0.0003	—0.0007	—0.0026
15	Calcium sulphate (dry)	0.0045	0.0032	0.0112	0.0080	0.0056	0.0073	0.0061	0.0057
11	Dry	0.0047	0.0035	0.0077	0.0098	0.0061	0.0063	0.0090	0.0072
	Gain (+) or loss (—)	—0.0002	—0.0003	+0.0035	—0.0018	—0.0005	+0.0010	—0.0029	—0.0015
5	Calcium sulphate (moist)	0.0061	0.0058	0.0114	0.0095	0.0039	0.0081	0.0061	0.0058
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	+0.0014	+0.0017	+0.0044	—0.0016	—0.0015	+0.0006	—0.0019	—0.0014
Aver. gain (+) or loss (—)		+0.0006	+0.0007	+0.0040	—0.0017	—0.0010	+0.0008	—0.0024	—0.0015

[1] Dry.

increases the effect of the calcium carbonate in decreasing the amount of chemically available plant food present.

Calcium sulphate increases chemically available phosphoric acid in each soil; it decreases potash in two soils, and increases it in one.

The increase in phosphoric acid dissolved from soil 1787 is very striking, being over 35 per cent. The solution was darker from the presence of more dissolved iron.

The decrease in dissolved potash is 15 to 25 per cent. The effect of calcium salts seems certainly to decrease the real or apparent chemically available potash as measured by N/5 or N/50 nitric acid, as a rule, the exception being soil 1786, in which the increase (moist) was about 40 per cent. This statement seems to be in conflict with the general opinion that calcium salts liberate potash; however, this liberation refers to aqueous solution, and does not refer to nitric acid solution, so that the conflict is not real.

Effect of Decaying Vegetable Matter.

These samples were provided with sawdust or starch and kept moist so as to allow decomposition. Two corrections were made in the results; first they were calculated to a soil containing the original amount of ignition residue, thus eliminating the effect of varying quantities of organic matter, and second, the potash in the starch or sawdust was subtracted. This correction was certainly too high in the case of the sawdust, as not half of it had decayed, but nevertheless, the results show plainly the effect of the organic matter.

The results are presented in Table III. First is to be noted an average loss of chemically available phosphoric acid (measured by N/5 nitric acid). Possibly the phosphoric acid enters into combination with the humus.

Next will be observed a very decided increase in chemically available potash. The increase is greatest with the poor soil, 1788, being nearly 100 per cent; with soil 1787 the increase is about 35 per cent. These figures show that considerable changes may take place in chemically available potash in the presence

Table III.—Effect of Organic Matter on Phosphoric Acid (P) and Potash (K).

Sample No.	Treatment.	Soil 1786.		Soil 1787.			Soil 1788.		
		P. Per cent.	K N/5. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent.	P. Per cent.	K N/5. Per cent.	K N/50. Per cent
7	Starch (moist)	0.0039	0.0053	0.0059	0.0154	0.0076	0.0060	0.0153	0.0084
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0008	+0.0012	—0.0011	+0.0043	+0.0022	—0.0015	+0.0073	+0.0012
4	Sawdust (moist)	0.0041	0.0044	0.0072	0.0146	0.0057	0.0053	0.0165	0.0076
1	Moist	0.0047[1]	0.0041	0.0070	0.0111	0.0054	0.0075	0.0080	0.0072
	Gain (+) or loss (—)	—0.0006	+0.0003	+0.0002	+0.0035	+0.0003	—0.0022	+0.0085	+0.0004
	Aver. gain (+) or loss (—)	—0.0007	+0.0007	—0.0007	+0.0039	+0.0012	—0.0019	+0.0079	+0.0008

[1] Dry.

of organic matter. The decaying organic bodies act upon the soil, changing unavailable potash into available forms. The effect of stable manure would be to liberate potash, as well as to furnish plant food and change the physical properties of the soil. This may be a very important function of vegetable matter in the soil.

The presence of vegetable matter in a soil would have a decided effect on the chemically available plant food present at the beginning and at the end of the growing season.

Summary and Conclusions.

1. Availability of plant food, as measured by plant tests, includes four factors: chemical availability, physical availability, physiological availability, and weathering availability.

2. Chemically available plant food is that present in forms that can be taken up directly by plants.

3. Physical availability refers to enclosure in soil particles or protection of chemically available food.

4. Physiological availability refers to the difference in power of plants to assimilate food.

5. Weathering availability refers to the conversion of plant food into chemically available forms during the growing season of the plant.

6. The effect of weathering under different conditions was studied on three soils, the chemical available plant food being measured by N/5 or N/50 nitric acid. The results vary somewhat with the nature of the soil.

7. Moisture alone causes an average increase in chemically available potash and phosphoric acid in the soils. The increase is not large.

8. Calcium sulphate and calcium carbonate cause an average decrease in chemically available potash. Calcium carbonate causes a decrease in phosphoric acid, calcium sulphate an increase, which is especially large in one case.

9. The presence of calcium salts in a soil has a decided influence on the potash and phosphoric acid extracted by N/5 nitric acid.

10. Starch or sawdust, in decaying, decreases the chemically available phosphoric acid but in each case increases the potash, as much as 100 per cent in one case.

11. Stable manure is valuable not only for the plant food in it, but for its action in liberating potash.

12. Weathering availability cannot be entirely disregarded in considering available phosphoric acid and potash in soils, particularly when calcium sulphate or carbonate or much organic matter is present in the soil.

This investigation will be continued.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE MOLECULAR REARRANGEMENT OF AMINOPHENYLALKYL CARBONATES.

By Henry T. Upson.

PART III.[1]

The only derivative of this class of compounds that was known when this work was undertaken was aminophenylethyl carbonate, which was obtained by Ransom by the reduction of *o*-nitrophenyl ethyl carbonate. The latter, in turn, was readily obtained by the treatment of *o*-nitrophenol in alkaline solution with ethyl chlorformate. In preparing new compounds of the above class, the same general method was followed, varying the nature of the nitrophenol from which a start was made. The purification of the derivatives is a matter of considerable difficulty, and particular care was therefore bestowed on preparing the nitrophenols in a perfectly pure condition. In many cases long and complex processes of separation of isomeric nitro compounds were repeatedly used, to insure purity. Besides this precaution, it was found that the successful reduction of each nitrophenyl alkyl carbonate to the amine required a special study of the particular conditions under which a good yield of the amine could be obtained. In view of the instability of these amines, their liability to rearrangement and to saponification, such a result was not unexpected. In the following description of the compounds prepared, attention will therefore be paid particularly to the experimental details of this part of the method of preparation. The experience gained with rather a large number of such compounds made it possible, finally, to isolate 4-chlor-2-aminophenyl acetate (see Part IV.) as the first *o*-aminophenyl ester of an acid other than carbonic acid. Böttcher had been unable to isolate such an amine as an intermediate product in the reduction of *o*-nitrophenyl benzoate, and in this laboratory all previous attempts at the preparation of such a body had proved unsuccessful.

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[1] For Parts I. and II., *vide* Stieglitz and Upson : This Journal, 31, 458 (1904).

EXPERIMENTAL PART.

p-Nitrophenyl Methyl Carbonate was obtained by the action of methyl chlorformate on *p*-nitrophenol in alkaline solution. It is a white solid soluble in ether and alcohol (m. p. 111° to 112°). It was not analyzed but was identified by the reduction to the

Hydrochloride of p-Aminophenyl Methyl Carbonate,

$CH_3O_2C\overset{1}{O}C_6H_4\overset{4}{N}H_3.Cl$.—This was prepared by treating the *p*-nitro carbonate with stannous chloride and hydrochloric acid. There was some difficulty in getting the body pure; although after reduction a large yield of the white body was obtained by Ransom's method,[1] the substance invariably turned silver nitrate black, and figures obtained from different analyses did not agree. Enough of the pure hydrochloride to make the conductivity measurements was obtained as follows:

The white solid obtained by reducing the nitro body with stannous chloride was added slowly to potassium hydroxide which had been ground to powder and covered with 50 cc. of absolute ether, to which 1 cc. of water had first been added. The impure hydrochloride was stirred thoroughly through the potassium hydroxide, the ether decanted and dried, and hydrogen chloride passed in. The white precipitate which formed was the pure hydrochloride, as is shown by the analysis.

For this, and the other hydrochlorides which will be described, the analyses were made by titration with N/10 silver nitrate solution, potassium chromate being used as indicator. The solutions were first neutralized with sodium carbonate.

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[1] This JOURNAL, 23, 48 (1900).

0.2111 gram substance required 10.39 cc. N/10 $AgNO_3$.

	Calculated for $C_8H_{10}O_3NCl$.	Found.
Cl	17.41	17.44

The body showed no tendency to rearrange when left in water for many hours.

o-Nitrophenyl methyl carbonate obtained from *o*-nitrophenol and methyl chlorformate is a yellow mobile oil.

Hydrochloride of o-Aminophenyl Methyl Carbonate, $CH_3O_2CO\overset{1}{C}_6H_4\overset{2}{N}H_3Cl$, was prepared by reducing the oil with tin and hydrochloric acid in the cold.[1] The mixture was added to concentrated cold alkali, extracted with ether, and the extract precipitated with dry hydrogen chloride. The yield of the pure white solid was 80 per cent.

0.2562 gram substance required 12.56 cc. N/10 $AgNO_3$.

	Calculated for $C_8H_{10}O_3NCl$.	Found.
Cl	17.41	17.38

The tendency of this body to rearrange and the conclusions drawn from the conductivity measurements have been discussed in a previous paper.[2]

A large yield of *o*-nitro-*p*-cresol was obtained by nitrating *p*-toluidine, diazotizing the crude amine, and distilling the product with steam. The yield of the pure nitrocresol, melting at 34° C., was between 75 and 80 per cent. This method was found better and a larger yield was obtained than by the direct nitration of *p*-cresol.[3]

2-Nitro-4-methylphenyl Ethyl Carbonate, $\overset{2}{N}O_2C\overset{4}{H}_3C_6H_3.\overset{1}{O}CO_2C_2H_5$.—The addition of ethyl chlorformate to the alkaline solution of the nitrocresol should be slow and the mixture shaken. A yellow oil forms which solidifies on cooling. After crystallization out of alcohol it melts at 56°.

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[1] This JOURNAL, **23**, 43 (1900).

[2] Stieglitz and Upson: *Ibid.*, **31**, 458 (1904).

[3] Brasch and Freyss: Ber. d. chem. Ges., **24**, 1960 (1891).

0.1904 gram substance gave 0.3696 gram CO_2 and 0.0844 gram H_2O.

	Calculated for $C_{10}H_{11}O_5N$.	Found.
C	53.33	52.93
H	4.89	4.93

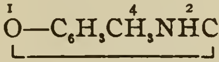
3-Methyl-6-oxyphenylurethane, $\overset{3}{C}H_3(O\overset{6}{H})C_6H_3.\overset{1}{N}HCO_2C_2H_5$.—Ten grams of 2-nitro-4-methylphenyl ethyl carbonate were dissolved in alcohol, 25 cc. concentrated alcohol added, and then slowly 12 grams granulated tin. After standing an hour the solution was filtered and an equal volume of water added. The mixture was allowed to stand over night and the following morning a quantity of white needles had formed. These were soluble in alkali, insoluble in acid, and melted after crystallization from alcohol at 101° C. The crystals continued to form slowly for several days.

A more rapid method for the preparation is as follows: Ten grams of the *o*-nitro-*p*-methylphenyl ethyl carbonate were placed in a flask with 24 cc. concentrated hydrochloric acid and 14 grams of powdered tin added slowly, the vessel being kept cold. Towards the end of the reduction the solution was allowed to come to ordinary temperature. As soon as the solution became clear it was filtered through glass wool, and after the addition of an equal volume of water, was heated to boiling for a few minutes. On cooling, a solid separated which, recrystallized from alcohol, melted at 101°. If care was not taken to avoid heat during the reduction, a body was invariably obtained which melted constantly at 77°, and an analysis did not give figures corresponding to any possible constitution, nor could it be proved to be a mixture by fractional crystallization. It was afterwards found, however, to be a mixture of carbonylaminocresol (m. p. 128°), and the urethane melting at 101°. These two bodies mixed in equal quantities melt at 77°.

0.1408 gram substance gave 0.3172 gram CO_2 and 0.0855 gram H_2O.

	Calculated for $C_{10}H_{13}O_3N$.	Found.
C	61.53	61.45
H	6.66	6.74

To fully establish the constitution of the urethane melting at 101° it was prepared from the hydrochloride of *o*-aminocresol and ethyl chlorformate. One gram of the salt was suspended in absolute ether and a slight excess of sodium carbonate, dissolved in a little water, was added. After being shaken with the ethereal solution, which had now become slightly brown, the water was separated and 0.5 molecule of ethyl chlorformate added slowly. After filtration and evaporation of the ether a solid remained which, without recrystallization, melted at 101°. Mixed with the urethane prepared by the rearrangement method there was no depression of the melting-point. The properties of this body in other respects were identical with those of the rearranged body formed by the reduction of the nitrocresyl carbonate.

Carbonyl-o-amino-p-cresol,  $\underbrace{\overset{1}{O}—C_6H_3C\overset{4}{H}_3N\overset{2}{H}CO}$.—To prove that in the preparation of the urethane by either of the above methods no alcohol had been lost, and carbonyl-*o*-amino-*p*-cresol formed—a reaction to which these urethanes are particularly liable—the urethane was heated carefully in an Anschütz distilling-flask. At a temperature above 110° decomposition took place and a liquid distilled over which the iodoform test proved to be alcohol. The heating was continued until no further decomposition took place and the contents of the flask were poured while still hot into an evaporating-dish. The liquid solidified at once to a very hard mass. This was ground into a powder, covered with water, and heated to boiling with bone-black. It was filtered while still hot, and white needles separated out of the filtrate while cooling. The needles were recrystallized out of hot water and melted sharply at 128°. Mixed with the body that melted at 101°, the melting-point was 77°. The carbonyl body is soluble in alcohol, ether and chloroform.

0.1539 gram substance gave 13.5 cc. N. at 26°.5 and 753 mm.

	Calculated for $C_{10}H_7O_2N$.	Found.
N	9.39	9.60

The Hydrochloride of 2-Amino-4-methylphenyl Ethyl Carbonate, $C_2H_5O_2\overset{1}{C}OC_6H_3\overset{4}{C}H_3\overset{2}{N}H_3Cl$.—In the first attempt to reduce the 2-nitro-4-methylphenyl ethyl carbonate, an alcoholic solution of the nitrocarbonate was used. This was done because, at the low temperature at which the experiment was to be carried out, the reduction was very slow. Previous experiment had shown that the amine would quickly suffer rearrangement, and it was important to have the reduction completed as soon as possible. The attempts, however, to isolate the amine hydrochloride after reduction in alcoholic solution were unsuccessful, because, as was afterwards found out, the amine hydrochloride is quite soluble in ether containing alcohol, and could therefore not be precipitated from the ethereal solution by the method which we used.

The following method gave a yield of 70 per cent of the pure amine hydrochloride. Two grams of the nitro compound were covered with 15 cc. of concentrated hydrochloric acid and cooled to about 10°. More than the calculated amount of granulated tin was added in small portions, the vessel being constantly shaken and the nitrocarbonate kept as finely divided as possible by rubbing with a glass rod. The temperature was not allowed to rise above the temperature of the hand. If the reduction is slow, the entire vessel will fill with a white mass which contains both organic and inorganic matter and is probably a tin double salt. If filtration is made after the reduction has been going on but for a short time, the precipitation of the tin double salt may be avoided. The best results, however, were obtained by allowing the reduction to continue until all of the nitrocarbonate had disappeared. The contents of the vessel were then cooled and added slowly to a very cold solution of 50 grams potassium hydroxide dissolved in 50 cc. of water. The mixture was extracted a number of times with absolute ether and dried with solid potassium hydroxide. Into the filtrate a slow stream of dry hydrogen chloride was passed, and a copious white precipitate was formed. This was filtered and dried at once on a clay plate in a desiccator. It is soluble in alcohol and dilute acid, and melts with decomposition at 135° to 137°.

0.1545 gram hydrochloride required 6.75 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_3NCl$.	Found.
Cl	15.34	15.44

The reduction was also carried out with concentrated hydrochloric acid and zinc dust. The result was in general the same as that obtained with granulated tin.

One-half gram of the hydrochloride was dissolved in as little water as possible and a concentrated solution of chlorplatinic acid added. In a few minutes the chlorplatinate formed as a yellow precipitate. This was filtered and washed with ether containing a little alcohol. The chlorplatinate is insoluble in ether, but soluble in alcohol. It melted above 171°, with blackening.

0.0140 gram substance gave 0.0034 gram Pt.

	Calculated for $C_{20}H_{30}O_6N_2PtCl_6$.	Found.
Pt	24.28	24.28

3-Methyl-6-oxyphenylurethane, $\overset{3}{C}H_3(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was dissolved in water and in a very short time white needles separated from the solution. These continued to form for more than twenty-four hours. The crystals melted at 101°, and, mixed with the urethane prepared as above, showed no depression of the melting-point. Other properties were also identical. This is in fact the best and quickest method for obtaining perfectly pure 3-methyl-6-oxyphenylurethane.

2-Nitro-m-cresol (m. p. 56°) was prepared by nitrating *m*-cresol in glacial acetic acid solution at a low temperature with fuming nitric acid and distilling the product with steam.[1]

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[1] Staedel and Kolb: Ann. Chem. (Liebig), **259**, 210 (1890).

2-Nitro-5-methylphenyl Ethyl Carbonate.—From an alkaline solution of the nitrocresol (m. p. 56°) and ethyl chlorformate a yellow oil separated which solidified when the vessel was cooled to —5°, but remained an oil at ordinary temperatures. Allowed to stand with a solution of potassium hydroxide it becomes red, showing a gradual saponification to the potassium salt of *o*-nitro-*m*-cresol.

0.3030 gram substance gave 17.55 cc. N at 25° and 730 mm.

	Calculated for $C_{10}H_{11}O_5N$.	Found.
N	6.22	6.24

Hydrochloride of 2-Amino-5-methylphenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}C_6H_3\overset{5}{C}H_3\overset{2}{N}H_3Cl$.—Two grams of the carbonate were reduced by the method described above for the isomeric compound and the hydrochloride of the amine was isolated in the same way. The yield was 60 to 70 per cent.

0.1695 gram substance required 7.35 cc. of N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_3NCl$.	Found.
Cl	15.34	15.37

The hydrochloride (0.4 gram) was dissolved in a very little water and a concentrated solution of chlorplatinic acid was added. A yellow precipitate formed which was filtered and washed with ether containing a little alcohol.

0.0210 gram chlorplatinate gave 0.0051 gram Pt.

	Calculated for $C_{20}H_{30}O_6N_2PtCl_6$.	Found.
Pt	24.28	24.27

4-Methyl-6-oxyphenylurethane, $\overset{4}{C}H_3(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride of the amine was treated with water. The entire solid went into solution at once, but on standing crystals began to form and continued to form for several hours. The crystals were soluble in alcohol, ether, and chloroform, insoluble in acid, but soluble in alkali. They melted, after recrystallization from boiling water, at 95°.

0.1295 gram substance gave 0.2915 gram CO_2 and 0.0781 gram H_2O.

	Calculated for $C_{10}H_{13}O_3N$.	Found.
C	61.53	61.39
H	6.66	6.71

2-Nitro-6-methylphenyl ethyl carbonate was obtained from *o*-nitro-*o*-cresol[1] (m. p. 70°) as a yellow oil. This was extracted with ether which was allowed to evaporate and, on cooling, the oil crystallized to yellow needles. For purification they were dissolved in alcohol and precipitated by water. 2-Nitro-6-methylphenyl ethyl carbonate readily remains an oil at ordinary temperatures, but the pure crystals showed a melting-point of 32° to 33°. A slight impurity prevents solidification to a great extent. Five grams of the oil were kept in cold winter weather for more than a week below 0° without solidifying. The first combustion gave figures which were high for nitrogen, but after two crystallizations from alcohol a pure body was obtained.

0.3554 gram substance gave 21.5 cc. N at 24° and 724 mm.

	Calculated for $C_{10}H_{11}O_5N$.	Found.
N	6.22	6.50

Hydrochloride of 2-Amino-6-methylphenyl Ethyl Carbonate, $C_2H_5O_2CO\overset{1}{C}_6H_3\overset{6}{C}H_3\overset{2}{N}H_3Cl$.—Considerable difficulty was experienced in reducing 6-methyl-2-nitrophenyl ethyl carbonate. This may have been due to the quality of tin which was used at this stage of the experiment,[2] or to a failure to find the proper temperature at which the reduction could be carried out. The final method, which gave about 65 to 70 per cent yield of the amine hydrochloride was as follows:

One gram of the carbonate (m. p. 32°) was covered with 12 cc. concentrated hydrochloric acid and cooled. An excess of granulated tin was added and the whole shaken and kept cold. (A reduction was afterwards carried out at ordinary temperature with a good result except a slight brown appearance of the final product.) After a time the vessel filled with a white solid which was added slowly to a very cold solution of potassium hydroxide (1 : 1). The dried ethereal extract gave with dry hydrogen chloride the salt as a white precipitate. A little alcohol in the ether or the presence of traces of water diminishes the yield. The hydrochloride is very soluble in water, soluble in alcohol, but insoluble in ether.

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[1] A. W. Hofmann and Miller: Ber. d. chem. Ges., **14**, 561 (1881); R. Hirsch: *Ibid.*, **18**, 1512 (1885).

[2] The quality of the tin used had quite an influence upon the result of the reductions carried out in this work. Recourse has been had to three separate shipments of granulated tin. The last, which was obtained from Kahlbaum, gave much the best results.

0.2022 gram substance required 8.84 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{14}O_3NCl$.	Found.
Cl	15.34	15.49

A saturated solution of chlorplatinic acid was added to a saturated solution of the hydrochloride. A yellow precipitate formed which, after being washed with ether containing a little alcohol and dried in a vacuum-desiccator, was analyzed.

0.351 gram substance gave 0.0850 gram Pt.

	Calculated for $C_{20}H_{30}O_6N_2PtCl_6$.	Found.
Pt	24.28	24.22

5-Methyl-6-oxyphenylurethane, $\overset{5}{C}H_3(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride of the amine dissolved in water gradually gave white needles on standing. These were soluble in alcohol and ether, insoluble in acid, but soluble in alkali. They melted after crystallization from hot water at 74° to 76°.

0.2051 gram substance gave 0.4610 gram CO_2 and 0.1255 gram H_2O.

	Calculated for $C_{10}H_{13}O_3N$.	Found.
C	61.53	61.31
H	6.66	6.80

The 4-chlor-2-nitrophenol used for the following experiments was prepared both by the nitration of the crude product obtained by the chlorination of phenol according to the method of Faust and Saame,[1] and also by nitration of pure *p*-chlorphenol. In both cases the body melting at 87° was obtained, but it was found, owing to the impurities in the crude product, that we could save time by first preparing the pure chlorphenol and nitrating afterwards.

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[1] Ann. Chem. (Liebig), Suppl., 7, 191 (1870).

4-Chlor-2-nitrophenyl Ethyl Carbonate.—Ten grams 4-chlor-2-nitrophenol were dissolved in a slight excess of potassium hydroxide solution and heated until all was in solution. A little more than 1 molecule of ethyl chlorformate was added slowly, with shaking. A light-yellow oil formed, which crystallized on cooling. It was filtered and washed with dilute potassium hydroxide solution, afterwards with water, and finally crystallized out of hot alcohol. An almost white solid was obtained, which melted at 60°.

0.3421 gram substance gave 18 cc. N at 21° and 745 mm.

	Calculated for $C_9H_8O_5NCl$.	Found.
N	5.72	5.91

The Hydrochloride of 4-Chlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}\overset{4}{Cl}C_6H_3\overset{2}{N}H_3Cl$.—In the first effort to reduce the carbonate with tin and hydrochloric acid in the cold, it was found that the reduction was very slow and the final product impure. The reduction could, however, be carried out much more rapidly at ordinary temperature, and the following method gave a 70 per cent yield of the pure product:

Three grams of carbonate were covered with 15 cc. of concentrated hydrochloric acid and cooled to about 10°. More than the calculated amount of granulated tin was added in small quantities and the vessel shaken, care being taken not to allow too much heat to generate. The solution cleared up somewhat, but after more than an hour the vessel filled with a white solid. This white body was added slowly with shaking to a very cold solution of 50 grams potassium hydroxide in 50 cc. water. The ethereal extract, treated in the same way as in previous cases, gave the hydrochloride as a white precipitate clinging somewhat to the sides of the vessel. It was filtered and dried on a clay plate in a desiccator. The body is fairly soluble in concentrated hydrochloric acid and glacial acetic acid, but insoluble in water and in alkali. It is soluble in alcohol, insoluble in benzene and chloroform. For analysis the solid was covered with water, the mixture carefully heated to about 75°, and after being cooled titrated with silver nitrate solution, potassium chromate being used as indicator.

0.1467 gram substance required 5.85 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{11}O_3NCl_2$.	Found.
Cl	14.06	14.13

Two parts of the hydrochloride were dissolved in as little absolute alcohol as possible, and 1 part of a concentrated absolute alcohol solution of chlorplatinic acid added. The mixture was rubbed and stirred for a short time, and then an excess of absolute ether was added. An almost quantitative yield of yellow needles was precipitated. They decomposed somewhat at about 140°, and softened at 175° to 180°.

0.0675 gram chlorplatinate gave 0.0157 gram Pt.

	Calculated for $C_{18}H_{22}O_6N_2PtCl_8$.	Found.
Pt	23.17	23.30

A remarkable property of the hydrochloride of 4-chlor-2-aminophenyl ethyl carbonate, compared with the bodies of the series described above, is its insolubility in water. The other hydrochlorides dissolve instantly in water at 0°. The hydrochloride of *p*-chlor-*o*-aminophenyl ethyl carbonate, covered with water at 25°, showed practically no tendency to dissolve, and only when heated to 92° did it go into solution, and then, no doubt, only because it had been rearranged.

3-Chlor-6-oxyphenylurethane, $\overset{3}{Cl}(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was covered with about 50 cc. of water and heated to boiling. At about 75° a brown oil formed which became gradually coated with white crystals. By frequent shaking the oil was completely changed to this white mass, which floated throughout the liquid. After the addition of more water the liquid was boiled, then cooled, and the white mass filtered. This, after drying, melted sharply at 136° to 137°. It was insoluble in acid, but soluble in alcohol, ether, and alkali, showing a decided change from the original amine hydrochloride.

0.1562 gram substance gave 0.2844 gram CO_2 and 0.0682 gram H_2O.

	Calculated for $C_9H_{10}O_3NCl$.	Found.
C	50.09	49.66
H	4.68	4.75

The rearranged body may also be obtained if the hydrochloride is covered with water and allowed to stand for a number of days at ordinary temperature.

As this was the first of the rearranged bodies containing a chlorine atom that we had obtained, a synthesis of the body was undertaken. The method used was to treat 4-chlor-2-aminophenol with ethyl chlorformate at ordinary temperature. The hydrochloride of this amine has been described by Faust and Saame,[1] but we were unable to obtain the body entirely free from tin by their method. The following method was used :

Two grams 4-chlor-2-nitrophenol (m. p. 87°) were covered with 15 cc. concentrated hydrochloric acid and the calculated amount of granulated tin added slowly, the solution being warmed a little. After a short time a white precipitate formed. When the reduction was complete the contents of the vessel were cooled, the liquid decanted, and the solid redissolved in water. After the tin was precipitated with hydrogen sulphide the solution was evaporated and the pure hydrochloride crystallized out.

One gram of the hydrochloride was suspended in ether in a separatory-funnel, and a slight excess of sodium carbonate, dissolved in a very little water, added. The water solution was separated from the ether and the calculated amount (0.5 molecule) of ethyl chlorformate added in small quantities. After the ether had evaporated a residue remained which melted at 136°, and mixed with the urethane formed by rearrangement, as prepared above, it caused no depression of the melting-point. The other properties were also identical with those of the rearranged body. The urethane was found to be unusually stable on being heated. Two grams 3-chlor-6-oxyphenylurethane were placed in a small Anschütz distilling-flask and heated slowly in a metal-bath. Up to 200° there was very little decomposition. Above 200° decomposition began. Alcohol distilled over, and, tested, gave iodoform. The heating must be carried out very slowly and the temperature kept at 230° for a considerable time. No effort was made to distil the carbonyl body over into the neck of the Anschütz apparatus, but after the decomposition was complete the residue was allowed to solidify and was dissolved in sodium hydroxide solution. The anhydro base was reprecipitated with hydrochloric acid, filtered, and crystallized several times from hot water. White needles were obtained which melted at 184° to 185°. If the decomposition was not complete, mixtures were obtained which melted at from 122° to 155°. Analysis proved the body to be carbonyl-4-chlor-2-aminophenol.

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[1] Ann. Chem. (Liebig), Suppl., 7, 193 (1870).

0.3211 gram substance gave 24.28 cc. N at 22° and 742 mm.

	Calculated for $C_7H_4O_2NCl$.	Found.
N	8.28	8.40

o-Chlorphenol (b. p. 176°) was prepared from the mixture obtained by the chlorination of phenol. The method of Faust and Müller,[1] as improved by Varnholt,[2] was used. It was found that the repeated distillation spoken of by Faust and Müller, for separating the isomers, can be avoided if a Glinsky tube is used and the distillation carried on very slowly. A yield of about 30 per cent of the oil, boiling at 176°, was obtained.

To 50 grams of *o*-chlorphenol[3] more than the calculated amount of nitric acid (sp. gr. 1.36), which had been diluted with an equal volume of water, was slowly added. A red oil formed, which became solid after twenty-four hours. This was collected, washed, and distilled with steam. The body obtained was practically pure 6-chlor-2-nitrophenol.

6-Chlor-2-nitrophenyl ethyl carbonate was obtained as an oil which could not be solidified at —15°. At this temperature, however, the oil became very thick.

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[1] Ann. Chem. (Liebig), **173**, 303 (1874).
[2] J. prakt. Chem., [2], **36**, 22 (1887).
[3] Ann. Chem. (Liebig), **173**, 307 (1874).

Hydrochloride of 6-Chlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}C_6H_3\overset{6}{Cl}\overset{2}{N}H_3Cl$.—One gram of the carbonate was reduced in the usual way. In ten or fifteen minutes the solution became clear, and in a short time, with the evolution of some heat, the entire mass solidified. From this mass the amine hydrochloride was obtained as in the previous preparations. It formed a voluminous precipitate, which melted with decomposition at 126° to 127°. It is soluble in alcohol, insoluble in water and alkali, and not very soluble in acid. The yield was 70 to 80 per cent.

0.1359 gram substance required 5.4 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{11}O_3NCl_2$.	Found.
Cl	14.06	14.11

5-Chlor-6-oxyphenylurethane, $\overset{5}{Cl}(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was covered with about 50 cc. of water at 25°. It softened and collected in the bottom of the vessel in a large mass. Heated a little, it turned to a brown oil, and the oil gradually went into solution. On cooling, a white crystalline solid (needles) separated, which was soluble in alcohol, ether, and alkali, but insoluble in acid. The melting-point was 92° to 93°.

0.1722 gram substance gave 0.3136 gram CO_2 and 0.0745 gram H_2O.

	Calculated for $C_9H_{10}O_3NCl$.	Found.
C	50.09	49.68
H	4.68	4.81

p-Bromphenol was prepared by the freezing method of Hübner and Brenken,[1] as extended by Hand,[2] with this exception, however, that the purification was accomplished by distillation *in vacuo*. This was done because small yields were obtained when distilled at ordinary temperature, due to decomposition, caused by the presence of small quantities of moisture. At 60 mm. the *p*-bromphenol boiled at 150°.

4-Brom-2-nitrophenol (m. p. 88°) was prepared by the nitration of *p*-bromphenol in glacial acetic acid solution with fuming nitric acid in the cold. When nitration was complete, the contents of the vessel were poured into water, filtered, washed with water, and distilled with steam. The pure body (m. p. 88°) was obtained from the barium salt.

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[1] Ber. d. chem. Ges., 6, 171 (1873).

[2] Ann. Chem. (Liebig), **234**, 136 (1886).

4-Brom-2-nitrophenyl ethyl carbonate was obtained from an ethereal solution in large, transparent plates, which melted at 76°.

Hydrochloride of 4-Brom-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}C_6H_3\overset{4}{Br}\overset{2}{N}H_3Cl$.—One gram of the above carbonate, in a small vessel, was covered with 15 cc. of concentrated hydrochloric acid. After cooling, an excess of granulated tin was slowly added. The reduction was allowed to proceed slowly, and too much heat was not allowed to generate from the reaction. After a short time a white solid, of delicate appearance, which could be distinguished from the nitro body, began to appear, and in the course of an hour the entire vessel was filled with a pure, white, solid mass. The best results were not obtained when the reduction was carried out in the cold. The temperature, however, was not allowed to rise above 20°. When the reduction was complete, the solid mass was cooled with a freezing-mixture and added slowly to a very cold solution of 50 grams of potassium hydroxide in 50 cc. of water, and the amine and its hydrochloride obtained in the usual way. The yield was 70 to 80 per cent; the melting-point was 136° to 137°.

0.1952 gram substance required 6.41 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{11}O_3NClBr$.	Found.
Cl	11.95	11.73

3-Brom-6-oxyphenylurethane, $\overset{3}{Br}(\overset{6}{O}H)C_6H_3\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was covered with water and heated. Most went into solution at the boiling-point, and on cooling white needles, melting at 139° to 141°, were obtained. These were soluble in alcohol, ether, chloroform, and alkali, but insoluble in acid. The body may be prepared more quickly if the hydrochloride is dissolved in alcohol, a little water added, and the mixture allowed to stand a short time at ordinary temperature. On addition of an excess of water, white needles, melting at 140° to 142°, are precipitated.

0.2407 gram substance gave 0.3636 gram CO_2 and 0.0869 gram H_2O.

	Calculated for $C_9H_{10}O_3NBr$.	Found.
C	41.52	41.20
H	3.88	4.01

In the preparation of 4-chlor-2-nitrophenol by the method of Faust and Saame[1] the crude material obtained in nitrating the chlorinated phenol was first changed into the barium salt by boiling with barium carbonate. The purpose was to separate the 6-chlor-2-nitrophenol from the 4-chlor-2-nitrophenol, advantage being taken of the different solubilities of their barium salts. The method did not effect a complete separation, so the barium salts were covered with water, precipitated with hydrochloric acid, washed, and the product distilled with a strong stream of steam. In the condenser a yellow deposit formed, which did not melt when the water surrounding it was brought to the boiling-point. It could not be, therefore, 4-chlor-2-nitrophenol (m. p. 87°), nor 6-chlor-2-nitrophenol (m. p. 70°). It was collected and found to melt sharply at 121° to 122°. This is the melting-point of 4,6-dichlor-2-nitrophenol, but as 4-nitro-2,6-dichlorphenol melts at 125°, it was necessary to distinguish between these bodies in another way. The ethyl ether was prepared by converting the dichlornitrophenol (m. p. 122°) into the silver salt and treating this with ethyl iodide. The product dissolved in alcohol and precipitated by water melted at 29°, which is the melting-point of the 4,6-dichlor-2-nitrophenol ethyl ether prepared by Fischer.[2] The sodium and barium salts were also prepared and corresponded in properties to those described by Fischer.

It seemed, therefore, that in the chlorination of phenol quite a quantity of 2,4-dichlorphenol is formed, and this was afterwards verified by the isolation of a quantity of 2,4-dichlorphenol (b. p. 209° to 210°), from the crude product obtained in the chlorination of phenol.

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[1] *Loc. cit.*

[2] Ann. Chem. (Liebig), Suppl., 7, 188 (1870).

4,6-Dichlor-2-nitrophenyl ethyl carbonate was obtained from the phenol (m. p. 122°) as a yellow oil, which solidified on cooling to a slightly yellow body melting at 38° to 39°. The yield was not so large as in the case of the other nitrocarbonates and it has been found to be general in these experiments that where the hydroxyl group is surrounded, as in this body, by other groups, it is much more difficult to bring it into action with the acyl group—a fact which may be explained on the basis of stereochemical interference.

Hydrochloride of 4,6-Dichlor-2-aminophenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}.C_6H_2\overset{4}{Cl}\overset{6}{Cl}\overset{2}{N}H_3Cl$.—Some difficulty was experienced in isolating the reduction-product of the carbonate because of the ease with which the former saponifies when brought into the cold alkaline solution. In different preparations different colorations were observed from red to green, and the products did not give good analytical results. With the following method a pure white salt was obtained. As it is better to work with small quantities, three reductions of 1 gram each were carried on at the same time. In each small vessel 1 gram of the carbonate was placed and covered with 12 cc. of concentrated hydrochloric acid. Granulated tin was added in small quantities and the vessels shaken. The flasks were not allowed to become warmer than 30° during the reduction. When the reductions were complete and the vessels cooled, a white solid mass formed. The concentrated acid was then decanted and the solid, which contained some tin, was added in small quantities to a very cold solution of 50 grams of potassium hydroxide in 50 cc. of water. The hydrochloride obtained from the dry ethereal extract was white and was washed with ether free from alcohol, but containing a little water. The hydrochloride was soluble in alcohol but insoluble in water, alkali, or acid. It melted with decomposition between 132° and 135°.

0.2111 gram substance, covered with water and heated, after cooling required 7.26 cc. N/10 $AgNO_3$.

	Calculated for $C_9H_{10}O_3NCl_3$.	Found.
Cl	12.32	12.21

3,5-Dichlor-6-oxyphenylurethane, $Cl_2(OH)C_6H_2NHCO_2C_2H_5$, is formed very rapidly by rearrangement of the amine when the hydrochloride is dissolved in alcohol and a little water added to the solution. After a short time an excess of water precipitates the urethane. It melts at 125°.

0.2344 gram substance gave 0.3685 gram CO_2 and 0.0791 gram H_2O.

	Calculated for $C_9H_9O_3NCl_2$.	Found.
C	43.20	42.88
H	3.64	3.76

The urethane was also prepared by the action of ethyl chlorformate on 4,6-dichlor-2-aminophenol. It melted at 125°, and mixed with the body prepared by rearrangement showed no depression of melting-point. The two bodies are identical.

Since 4,6-dichlor-2-aminophenyl ethyl carbonate showed such an unusual tendency to rearrange, thus emphasizing the tendency of negative groups to hasten the molecular change, it seemed of interest to gain some further evidence as to the combined action of negative groups upon the rearrangement. 4-Chlor-6-brom-2-nitrophenol was therefore prepared. Ten grams 4-chlor-2-nitrophenol (m. p. 87°) was dissolved in glacial acetic acid and brominated at a high temperature, according to the method of Ling.[1] In this manner a quantitative yield of 4-chlor-6-brom-2-nitrophenol (m. p. 125°) was obtained.

4-Chlor-6-brom-2-nitrophenyl Ethyl Carbonate.—A known weight of the phenol was dissolved in a little more than the calculated amount of potassium hydroxide solution, and to this red solution a slight excess of ethyl chlorformate was added slowly with shaking. As in other cases where the hydroxyl group is surrounded, the reaction with ethyl chlorformate was not rapid, but after much shaking a yellow oil formed. This was extracted with ether and on evaporation yellow prisms remained. They were crystallized out of alcohol and melted at 48° to 49°.5.

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[1] J. Chem. Soc. (London), **55**, 583 (1889).

Hydrochloride of 2-Amino-4-chlor-6-bromphenyl Ethyl Carbonate, $C_2H_5CO_2\overset{1}{O}.C_6H_2\overset{4}{Cl}\overset{6}{Br}\overset{2}{N}H_3Cl$.—One gram of carbonate was treated with 12 cc. of concentrated hydrochloric acid and after cooling an excess of granulated tin was added. In a short time a flaky white substance began to form which clung to the sides of the vessel. The reduction in this case was slow, and it was not until after a considerable time that the yellow nitro body entirely disappeared. When the reduction was complete the entire contents of the vessel were poured slowly into 50 cc. of a very cold solution (1 : 1) of potassium hydroxide. The ethereal extract was red, and continued red after drying with solid potassium hydroxide. It was then filtered and dry hydrogen chloride passed in. The solution at first became colorless and no precipitate formed for some time, but finally, after considerable gas was passed in, a white precipitate formed. The yield was 60 per cent. The hydrochloride, filtered and washed with absolute ether and dried in a vacuum-desiccator, was analyzed (Analyses I. and II.).

The analysis did not give figures corresponding to the pure salt desired, and other preparations were made, using smaller quantities for the reduction and keeping the temperature very low and cooling the ether before making the extraction. In this manner the colorations of the ethereal solution were avoided, and the salt obtained purer than before, but not perfectly pure, as shown by the third analysis.

0.2312 gram substance required 8.9 cc. N/10 $AgNO_3$.
0.2145 gram substance required 7.56 cc. $AgNO_3$.
0.1921 gram substance required 6.01 cc. $AgNO_3$.

	Calculated for $C_9H_{10}O_3NCl_2Br$.	Found.		
		I.	II.	III.
Cl	10.68	13.71	12.50	11.11

The salt melted with decomposition at 131° to 132°. It is insoluble in water.

3-Chlor-5-brom-6-oxyphenylurethane, $\overset{3}{\mathrm{Cl}}\overset{5}{\mathrm{Br}}(\overset{6}{\mathrm{O}}\mathrm{H})\mathrm{C_6H_2}\overset{1}{\mathrm{N}}\mathrm{HCOC_2H_5}$.—One-half gram of the hydrochloride was dissolved in alcohol, an equal volume of water added, and the whole allowed to stand for a short time. On adding an excess of water a white precipitate formed. This was soluble in alkali and insoluble in acid. It melted at 116° to 118°.

0.1909 gram substance gave 0.2566 gram CO_2 and 0.0605 gram H_2O.

	Calculated for $C_9H_{10}O_3NClBr$.	Found.
C	36.66	36.65
H	3.08	3.46

4,6-Dibrom-2-cresol (m. p. 57°), was prepared by the bromination of *o*-cresol in glacial acetic acid solution in the presence of small pieces of iron[1] wire. 4-Brom-6-nitro-2-cresol (m. p. 88°) was prepared from it by treatment in glacial acetic acid with sodium nitrite, the product being distilled with steam and finally crystallized out of alcohol, according to the method of Zincke.[2] It was found that a somewhat better yield can be obtained if the dibrom body is allowed to stand over night with a slight excess of sodium nitrite before the addition of water.

4-Brom-2-nitro-6-methylphenyl Ethyl Carbonate.—Five grams of the cresol (m. p. 88°) were dissolved in a small excess of potassium hydroxide solution, and a slight excess of ethyl chlorformate was slowly added. As before, where the hydroxyl group is surrounded, the reaction was slow, but a yellow oil finally separated which, on cooling, solidified. This contained some of the unchanged nitrophenol, as was shown by the red color produced by addition of alkali, and the variation of melting-point from 44° to 55°, after repeated crystallizations from alcohol. To obtain the pure body the substance was washed repeatedly with dilute potassium hydroxide solution and finally with water. It is soluble in alcohol, ether, and chloroform and melts at 61° to 62°.

[1] J. prakt. Chem., [2], 38, 325 (1888).

[2] We are under obligations to Prof. Th. Zincke, who very kindly placed the dissertation of Wagner, 1899, at our disposal.

Hydrochloride of 2-Amino-4-brom-6-methylphenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}C_6H_2(\overset{6}{C}H_3)\overset{4}{B}r\overset{2}{N}H_3Cl$.—One gram of the pure carbonate was covered with 15 cc. of concentrated hydrochloric acid and an excess of granulated tin added. The vessel was not heated, but no attempt was made to keep it cold. A white solid formed throughout the liquid and after some time collected at the top of the liquid. After the reduction was complete the entire mass was cooled and added slowly to 50 cc. of a 1 : 1 solution of potassium hydroxide which had been cooled to —10°. This was extracted several times with absolute ether and dried with solid potassium hydroxide. Dry hydrogen chloride gave a white precipitate. It was washed with absolute ether and dried on a clay plate in a desiccator. Heated, it darkened at 137° to 143°, but did not melt until 173° to 178°, and then with decomposition. The hydrochloride is soluble in alcohol and insoluble in water.

0.2031 gram substance required 6.54 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{13}O_3NClBr$.	Found.
Cl	11.41	11.43

3-Brom-5-methyl-6-oxyphenylurethane, $(\overset{6}{O}H)\overset{3}{B}r(\overset{5}{C}H_3)C_6H_2\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was placed in a flask and covered with about 50 cc. of water. The water did not seem to wet the body, as in the case of the isomer, which will be described later. When heated, however, it went into solution more readily than the isomer. When cooled, a white solid separated, which was soluble in alkali and had the same general properties as the other urethanes which had already been prepared. The melting-point was 123°.

0.2127 gram substance gave 0.3392 gram CO_2 and 0.0873 gram H_2O.

	Calculated for $C_{10}H_{12}O_3NBr$.	Found.
C	43.77	43.5
H	4.42	4.56

2,6-Dibrom-4-cresol (m. p. 49) was prepared from *p*-cresol by bromination in glacial acetic acid solution with the calculated amount of bromine, according to the method of Glaus and Jackson.[1]

Ten grams of the brominated cresol were dissolved in a small amount of glacial acetic acid and slowly a slight excess of sodium nitrite was added. After a short time a yellow precipitate formed. When the reaction was complete, the contents of the vessel were poured into a large bulk of water, filtered, and washed. The yellow crystalline mass, after crystallization from alcohol, melted at 69°, and was 2-nitro-6-brom-4-cresol.

This body was also prepared from 2-nitro-4-cresol[2] by bromination with potassium bromate and an acid solution of potassium bromide. The yield, however, in this case was not so good as by the first method.

2-Nitro-4-methyl-6-bromphenyl Ethyl Carbonate.—Five grams of nitrobromcresol (m. p. 69°) were dissolved in slightly more than the calculated amount of potassium hydroxide solution, and slowly a small excess of ethyl chlorformate was added. A yellow solid formed which melted at from 65° to 75°. On shaking out with dilute potassium hydroxide solution the melting-point became constant at 84° to 85°. The reactivity of the ethyl chlorformate is here also interfered with, because of the enclosed position of the hydroxyl group, and a quantitative yield was not easily obtained.

Hydrochloride of 2-Amino-4-methyl-6-bromphenyl Ethyl Carbonate, $C_2H_5O_2C\overset{1}{O}C_6H_2(\overset{4}{C}H_3)\overset{6}{Br}\overset{2}{N}H_3Cl$.—One gram of the carbonate (m. p. 84°) was covered with 15 cc. concentrated hydrochloric acid and an excess of granulated tin added. The reduction was carried on at ordinary temperatures. When reduction was complete the contents of the vessel were treated as usual. The hydrochloride obtained from the ethereal solution was washed with absolute ether and dried on a clay plate in a desiccator. It is insoluble in water, but soluble in ether, to which a little alcohol has been added. The substance melted at 142° to 143°, with decomposition.

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[1] *Loc. cit.*

[2] Thiele and Eichwede : Ann. Chem. (Liebig), **311**, 375 (1900).

0.2311 gram substance required 7.43 cc. N/10 $AgNO_3$.

	Calculated for $C_{10}H_{13}O_3NClBr$.	Found.
Cl	11.41	11.40

3-Methyl-5-brom-6-oxyphenylurethane,

$\overset{3}{C}H_3\overset{5}{B}r(\overset{6}{O}H)C_6H_2\overset{1}{N}HCO_2C_2H_5$.—One gram of the hydrochloride was heated with about 50 cc. of water. A brown oil formed which did not go entirely into solution. Upon cooling, the oil solidified and melted at 83°. It was soluble in alcohol, ether, and alkali, but insoluble in acid.

0.2100 gram substance gave 0.3357 gram CO_2 and 0.0822 gram H_2O.

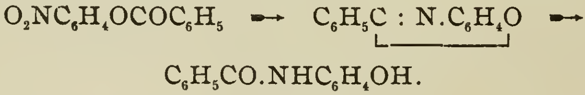
	Calculated for $C_{10}H_{12}O_3NBr$.	Found.
C	43.77	43.60
H	4.42	4.35

PART IV.

2-Amino-4-chlorphenyl Acetate.

Hübner and Stünkel,[1] in reducing *o*-nitrophenyl benzoate with a view to obtaining *o*-aminophenyl benzoate, found that from the alcoholic solution in which the reduction was carried on, an anhydrobenzenyl-*o*-aminophenyl base was in every case obtained. This compound, when boiled with water, went over into benzoyl-*o*-aminophenol. They ascribed the formation of the anhydro base as a primary product, instead of the expected aminophenyl benzoate to the great instability of the amino bodies.

Böttcher,[2] in repeating the work of Hübner and Stünkel, observed that by varying the temperature at which the experiment was carried out either the anhydro base or the benzoyl-*o*-aminophenol could be obtained at will. He suggested the following stages for the reaction :



$$O_2NC_6H_4OCOC_6H_5 \longrightarrow C_6H_5\underbrace{C : N.C_6H_4O}_{} \longrightarrow$$

$$C_6H_5CO.NHC_6H_4OH.$$

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[1] Ann. Chem. (Liebig), **210**, 384 (1881).

[2] Ber. d. chem. Ges., **16**, 631 (1883).

In a later work Böttcher,[1] trying to determine if this rearrangement is a perfectly general one, tried, among other experiments, a reduction of *o*-nitrophenyl acetate, thinking that the anhydro base, ethenylaminophenol would in like manner be formed. Trying the reduction with alcoholic ammonia and hydrogen sulphide in the cold, with tin and hydrochloric acid, and with zinc and acetic acid, he was unable to obtain either acetylaminophenol, the anhydro base, or aminophenyl acetate, as he thought, on account of the saponification of *o*-nitrophenyl acetate, in the process of the reduction, the acetate being supposedly much more unstable than the benzoate.

The experiments with the hydrochloride of 4-chlor-2-aminophenyl ethyl carbonate, which have been described above, and the surprising insolubility of this salt in water, suggested that if the chlorine in the para position should effect a similar insolubility of an acetate, it might be possible to prepare the hydrochloride of 4-chlor-2-aminophenyl acetate as the first body of its kind ever isolated. A study of it would determine the real nature of the processes by means of which an anhydro base or an acylaminophenol was always obtained by the reduction of the nitrophenyl acetates and benzoates. By the observation of minute precautions we have been able to isolate the hydrochloride of 2-amino-4-chlorphenyl acetate, although it proved to be readily soluble in water. In contact with water, it produces acetyl-2-aminochlorphenol, not by the successive loss and addition of water with the intermediate formation of an anhydro base, but by a molecular rearrangement according to

$$CH_3COOC_6H_3ClNH_3Cl \rightarrow HOC_6H_3ClNHCOCH_3 + HCl.$$

The free base, aminochlorphenyl acetate, was also obtained from its salt and observed to change spontaneously into the isomeric phenol. The anhydro base was prepared by the action of heat on acetylaminochlorphenol and compared with the amine.

4-Chlor-2-nitrophenyl Acetate.—Ten grams of 4-chlor-2-nitrophenol (m. p. 87°) were put in a flask with fused sodium acetate and an excess of acetic anhydride added. The mixture was heated for more than an hour, above 100°, in an air-bath, and shaken from time to time. On cooling, the entire mass solidified. It was covered with water, and an oil formed at the bottom of the vessel. After the water solution had been removed, the oil was washed several times with dilute potassium hydroxide solution, to dissolve any unchanged phenol. When placed in ice-water the oil solidified to an almost white solid. 4-Chlor-2-nitrophenyl acetate is quite soluble in benzol, chloroform, and ether, fairly soluble in alcohol, and may be precipitated from alcohol solution by water. It melts between 47° and 48°. It was identified by the reduction to

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[1] Ber. d. chem. Ges., **16**, 1933 (1883).

The Hydrochloride of 4-Chlor-2-aminophenyl Acetate, $ClNH_3C_6H_3ClOCOCH_3$.—In the first attempt to reduce the acetate, 1 gram was covered with 10 cc. concentrated hydrochloric acid, and more than the calculated amount of granulated tin was added in small quantities to the cold solution, which was kept at about 0°. After some time the solution became clear and was poured slowly into a solution of 50 grams of potassium hydroxide in 50 cc. water which had been cooled to —10° C. When the concentrated acid solution went into the cold potassium hydroxide, drop by drop, fumes arose which indicated a decomposition. The potassium hydroxide solution was extracted several times with ether, the extract dried with solid potassium hydroxide, filtered, and treated with dry hydrogen chloride; no precipitate was formed, and on evaporation to dryness no residue remained. It was evident that nothing had been taken up by the ether.

A second experiment was carried out exactly as above, with this exception, that a deep layer of absolute ether was placed over the potassium hydroxide solution. The ether and alkali were then cooled to —10° C. The cold acid solution containing the reduced product was poured, drop by drop, through glass wool upon the ether and shaken after each addition, the temperature not being allowed to rise above —5° C. The ether was decanted into a cold vessel containing some solid potassium hydroxide and two similar extraction with cold ether were made. After being dried for some time,[S] the ethereal solution was filtered into another cold vessel and dry hydrogen chloride run in. A pure white hydrochloride formed in a short time, which was filtered and placed on a clay plate in a vacuum-desiccator. Put into water, it went into solution for an instant, but then a white, oily body came out, insoluble in alkali, but soluble in concentrated acid. On standing in water for more than a day, it became crystalline, and was soluble in alkali, no longer soluble in acid, and melted at 176°. The hydrochloride, on the other hand, melts at 105° to 107°. It had been converted by a molecular rearrangement into acetyl-2-amino-4-chlorphenol, which, as will be shown below, melts at 176°. In the analysis of the hydrochloride it was warmed with some water to cause the rearrangement and the liberated hydrochloric acid was then titrated with standard alkali.

0.2468 gram substance (dried for twenty-four hours) required 10.64 cc. N/10 NaOH.

0.3222 gram substance (dried for two hours) required 14.02 cc. N/10 NaOH.

	Calculated for $C_8H_9O_2NCl_2$.	Found. I.	II.
Cl	15.96	15.40	15.52

The analysis indicated that the hydrochloride of 2-amino-4-chlorphenyl acetate had been isolated. As it gave a somewhat low chlorine value and the hydrochlorides of anhydro bases, which had hitherto always resulted from reductions of *o*-nitrophenyl acetates, have a well-known tendency to lose hydrochloric acid on standing, further evidence of the identity of the amine hydrochloride was sought. Its identity was confirmed by the preparation of a chlorplatinate and fully established by the preparation and study of the hydrochloride of the anhydro base itself. As expected, the latter proved to be quite a different body from the salt described above. The free bases were prepared from the two salts and also found to be different compounds, and the aminochlorphenyl acetate obtained from the hydrochloride, which has just been described, rearranged spontaneously into the isomeric acetylaminochlorphenol. In view of these facts the salt obtained as the first product of the reduction of the nitro compound has undoubtedly the constitution assigned to it.

A chlorplatinate of the base was obtained by the addition of a concentrated solution of chlorplatinic acid in absolute alcohol to a cold ethereal solution of freshly prepared amine. The yellow precipitate was washed with ether containing some alcohol and dried on a clay plate. It is insoluble in water, and rubbed with water no change of color or apparent decomposition takes place. It darkens at 120° and does not melt at 200°.

0.0256 gram substance gave 0.0064 gram Pt.

	Calculated for $C_{16}H_{18}O_4N_2PtCl_8$.	Found.
Pt	24.95	25.00

2-Amino-4-chlorphenyl Acetate, $H_2N.C_6H_3Cl(OCOCH_3)$.—A little of the ethereal solution of the amine, prepared as described above, was allowed to evaporate. White needles, turning a little red on standing in the air, remained. They melted at 73° to 74°. The addition of some of the anhydro base, described below, whose melting-point is 54°, lowered the melting-point of the amine below 40°. The amine is soluble in acids, insoluble in alkalies, soluble in chloroform and benzene, but not very soluble in low-boiling ligroin. The base was allowed to stand for a day and the melting-point again taken. The substance fell together a little at 73°, but it did not melt until 176°, the melting-point of acetylaminochlorphenol. The aminochlorphenyl acetate had evidently suffered a molecular rearrangement according to

$$CH_3COOC_6H_3ClNH_2 \rightarrow HOC_6H_3ClNHCOCH_3.$$

Acetyl-2-amino-4-chlorphenol, $CH_3CONH.C_6H_3Cl(OH)$.—In an endeavor to prepare a quantity of the rearranged body melting at 176°, for purposes of analysis and further investigation, some surprising results were obtained. Two grams of the 4-chlor-2-nitrophenyl acetate were reduced with powdered tin and concentrated hydrochloric acid, the solution being kept cold, as above. After all had gone into solution it was poured through glass wool into about two volumes of water at ordinary temperature. The entire vessel of water became milky white, and when filtered, the filter-paper was covered with a white, thick, oily substance. The oil was insoluble in alkali, fairly soluble in concentrated acid, and when rubbed with alcohol and ether went into solution. When some of the oil placed in a test-tube was dissolved in ether and dry hydrogen chloride run in, a white precipitate formed. This hydrochloride is not soluble in water and turns brown on standing in the air. Heated in a melting-point tube, it became brown below 100° C., but did not melt until 233° to 235° C. If allowed to stand for more than a day in water, it became crystalline and melted sharply at 176° C. We expect in a later work to investigate the oil more carefully. It may be an intermediate product in the rearrangement of the amine. Its evident impurity and the fact that it contains inorganic matter, led us to abandon it here as not leading to a direct knowledge of the identity of the supposed 4-chlor-2-aminophenyl acetate. An analysis of the body melting at 176° was made.

0.2748 gram substance gave 0.5188 gram CO_2 and 0.1088 gram H_2O.

	Calculated for $C_8H_8O_2NCl$.	Found.
C	51.73	51.48
H	4.35	4.40

The body is soluble in alkali and reprecipitated by acid and is undoubtedly acetyl-2-amino-4-chlorphenol. It was also prepared synthetically as follows: One gram of the hydrochloride of 2-amino-4-chlorphenol was mixed thoroughly with 1 gram of fused sodium acetate and covered with 3 grams of acetic anhydride. This mixture was heated to boiling under an inverted condenser for four hours. On adding water, a part did not go into solution, and this, on purification, melted at 176° C. Mixed with the acetyl body prepared by the above method, it caused no depression of the melting-point. It had also, in other respects, the properties of acetyl-2-amino-4-chlorphenol.

Ethenyl-4-chlor-2-aminophenol, $CH_3\underline{C : N.C_6H_3ClO}$. — The anhydro base was prepared for comparison of its hydrochloride with the hydrochloride of 4-chlor-2-aminophenyl acetate. One gram acetyl-2-amino-4-chlorphenol was placed in an Anschütz distillation-bulb and heated carefully. It melted at 176° and soon afterward drops of water were given off which collected in the side tube. At 218° to 220° the anhydro base distilled over. The distillate was poured upon a watch-crystal and placed over solid potassium hydroxide in a vacuum-desiccator. White needles formed at once. They melted sharply at 53° to 54°. These crystals have a peculiar, pleasant odor. They are soluble in dilute acid, insoluble in alkali, soluble in ether, alcohol, benzene, and chloroform. One-half gram was dissolved in absolute ether and dry hydrogen chloride run in. After some time a white precipitate formed. This was filtered, washed with absolute ether, and dried. This hydrochloride is soluble in dilute acid, insoluble in alkali, and not very soluble in water. It is soluble in alcohol and chloroform, but very little soluble in benzene. It does not give the peculiar milky appearance shown by the hydrochloride of 4-chlor-2-aminophenyl acetate when covered with water. It melted at 129° to 130°.5.

0.1928 gram of the hydrochloride was weighed at once after precipitation, covered with water, and the acid titrated with N/10 sodium hydroxide.

	Calculated for $C_8H_7ONCl_2$.	Found.
Cl	17.37	17.34

This hydrochloride gave off hydrogen chloride on standing, and, after two days, again melted at 53° to 54°, having returned to the anhydro base. The hydrochloride was mixed with the hydrochloride of 4-chlor-2-aminophenyl acetate. The mixture melted below 100° C.

The anhydro base (0.25 gram) was dissolved in absolute ether and chlorplatinic acid in absolute alcohol solution added.

The yellow precipitate was filtered and washed with ether containing some alcohol. The chlorplatinate is with difficulty soluble in alcohol, insoluble in benzol, chloroform, and ligroin. Covered with water and rubbed, it turned white with evident decomposition. Heated in a melting-point tube, it did not darken or melt at 220° C.

0.0202 gram chlorplatinate gave 0.0053 gram Pt.

	Calculated for $C_{16}H_{14}O_2N_2PtCl_8$.	Found.
Pt	26.16	26.20

The evidence is conclusive that with proper precautions an *o*-aminophenyl acetate can be isolated as the primary reduction-product of the *o*-nitrophenyl acetates. Hübner, Stünkel, Böttcher, and others, who have studied the reduction of these bodies, failed to obtain the amines, most likely because heat was probably allowed to generate during the reduction, with a consequent change of the amine by rearrangement into the oxyacetanilide or by a loss of water into an anhydro base.

I wish here to express my thanks to Professor Stieglitz for the careful attention he has given to each part of this work.

THE ACTION OF HYDROGEN PEROXIDE UPON ANHYDRIDES AND THE FORMATION OF ORGANIC ACID, PEROXIDES, AND PERACIDS.

BY A. M. CLOVER AND A. C. HOUGHTON.

Nef[1] has shown that pure hydrogen peroxide and acetic anhydride reacting with each other yield acetic peroxide. Baeyer[2] found that the same substance was formed by the action of acetic anhydride upon an aqueous solution of hydrogen peroxide. Neither of these authors attempt to explain the reaction which takes place and one might be led to suppose that the peroxide was formed by the direct addition of oxygen to the anhydride. In considering the reaction of hydrogen peroxide upon benzoyl acetyl oxide, however, Nef assumes the following reaction to take place :

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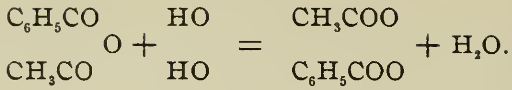
[1] Ann. Chem. (Liebig), **298**, 287.

[2] Ber. d. chem. Ges., **33**, 1569.



$$\begin{matrix}C_6H_5CO\\CH_3CO\end{matrix}O + \begin{matrix}HO\\HO\end{matrix} = \begin{matrix}CH_3COO\\C_6H_5COO\end{matrix} + H_2O.$$

In attempting to prepare other peroxides by the action of anhydrides upon hydrogen peroxide we have found that only the anhydrides of the simple acids react with hydrogen peroxide, *i. e.*, anhydrides which are acted upon by water. Even when the more complex and less soluble anhydrides are brought together with hydrogen peroxide in ethereal solution, there is no reaction.

From experimental facts which will be brought out later in this article, it will be seen that the action of hydrogen peroxide upon anhydrides is not a simple one: that the reaction is very similar to that of water upon anhydrides, and the formation of peroxides depends upon two distinct reactions.

Changes in Acetic Peroxide when Dissolved in an Aqueous Solution of Hydrogen Peroxide.

The changes which an aqueous solution of acetic peroxide undergoes have been previously studied by one of the authors in connection with G. F. Richmond.[1] It was found that the substance was hydrolyzed with the formation of acetic acid and acetic peracid, and it was shown that acetic peracid could be distinguished from acetic peroxide by its very rapid action upon potassium iodide. The action of acetic peroxide in dilute solution upon potassium iodide, if the latter be not in large excess, is so slow that the iodine liberated by the peracid may be estimated with little error.

We have found that when acetic peroxide is dissolved in a solution of hydrogen peroxide there is a similar change into peracid, but that the amount of peracid in the solution is more than can be accounted for by the reaction of the peroxide upon water; moreover, that there is a gradual loss of hydrogen peroxide in the solution, the active oxygen of which is found combined with the acetyl group. In order to follow these changes, it is necessary to be able to accurately estimate hydrogen peroxide, acetic peroxide, and acetic peracid in the presence of each other.

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[1] This JOURNAL, 29, 179.

In dilute solutions containing no mineral acid, the action of hydrogen peroxide, as well as acetic peroxide, upon potassium iodide, is so slow that with practice one may accurately estimate peracid by adding a drop or two of strong potassium iodide solution and titrating immediately with thiosulphate. If only a small amount of potassium iodide is added, there need be no especial hurry in making the titration; after the removal of the "immediate" iodine, the further liberation can be seen to be very slow. If too much potassium iodide is used it is necessary to operate quickly and to make a preliminary titration to obtain approximately the amount of thiosulphate required; the estimation may then be made quickly. In either case, after a little practice, one may satisfy himself of the accuracy of the result.

The estimation of hydrogen peroxide may be accurately made by adding to a large excess of dilute sulphuric acid (2N acid was used) and titrating with permanganate. It has been previously shown that peracids oxidize manganous salt to permanganic acid, and that this action interferes with the estimation as ordinarily made; however, in very dilute solution, which is strongly acidified, this action is so retarded that there is little error.

The following experiments illustrate the accuracy of the method:

Ten cc. of a solution of commercial hydrogen peroxide titrated with N/20 permanganate in the ordinary manner required 23.7 cc. A strong solution of pure acetic peroxide[1] was made and allowed to stand for four hours. At the end of this time the peracid in 1 cc. of the solution was represented by 6.1 cc. N/20 thiosulphate; the unchanged peroxide by 6.6 cc. Only a trace of hydrogen peroxide had been developed.

Separate portions, of 10 cc. each, of the above solution of hydrogen peroxide were then each diluted to 300 cc. with dilute sulphuric acid and cooled to 10°. To the first was then added 1 cc. of the above solution of acetic peroxide and peracid, to the second 2 cc., to the third 3 cc., and to the fourth 4 cc. These solutions were then titrated with N/20 permanganate.

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[1] The acetic peroxide used in this work was prepared according to the method of Clover and Richmond (*Loc. cit.*) and was recrystallized from ligroin just before using.

	Required. cc.
1	23.65
2	23.60
3	23.65
4	23.55

In the fourth solution the amount of active oxygen as peracid was nearly equal to that as hydrogen peroxide. To obtain accurate results it is necessary to make the titration quickly, and to do this it is necessary, in case the amount of hydrogen peroxide in the solution is unknown, to make a preliminary titration in order to obtain approximately the volume of permanganate required.

The acetic peroxide cannot be directly estimated, but may be obtained by difference after estimating the total active oxygen. This may be accurately done by dissolving in a small amount of 20 per cent acetic acid containing potassium iodide and allowing to stand for a half hour, then diluting and titrating with thiosulphate. Careful experiments with known quantities of hydrogen peroxide, acetic peroxide, and acetic peracid have shown that all of these substances may be accurately estimated in this way. A correction obtained from a blank solution may be applied.

A solution of commercial hydrogen peroxide containing 30.5 grams per liter was nearly saturated with pure acetic peroxide. The contents of the solution were estimated as quickly as possible after it was made and then at intervals. The temperature of the solution remained constant, 23°.

For the estimation of hydrogen peroxide 1 cc. of the solution was removed and diluted to 100 cc. Fifty cc. of this were removed, and after diluting to 300 cc. with dilute sulphuric acid, were titrated with N/20 permanganate, as already described. This number multiplied by 2 is the one given in the table.

For the estimation of peracid, 1 cc. of the solution was added to 300 cc. of water, a small amount of potassium iodide solution added, and the iodine liberated was titrated quickly with N/20 thiosulphate.

The total active oxygen contained in 1 cc. of the solution was determined by dissolving in 6 or 7 cc. of a 20 per cent solution of acetic acid containing potassium iodide, and allowing to stand for one-half hour. The solution was then diluted and the free iodine estimated with N/20 thiosulphate. Only a slight correction, amounting to about 2 drops of thiosulphate, is necessary.

The three portions to be estimated were removed from the original solution as quickly as possible after each other. After being diluted as described no further change takes place in the diluted solution during the time necessary to carry on the estimations.

Time in hours.	N/20 thiosulphate (immediate). cc.	N/20 thiosulphate total. cc.	N/20 permanganate. cc.	N/20 thiosulphate representing acetic peroxide. cc.
..	..	48.5	35.0	13.5
2	6.7	48.0	31.7	9.6
7	12.7	47.5	28.8	6.0
24	13.9	46.1	27.8	4.4

An inspection of these figures brings out the following facts:

(1) At the end of two hours the amount of active oxygen as peracid in the solution is just one-half of that originally present as peroxide. The formation of peracid is, therefore, much faster than in aqueous solution.[1]

(2) The amount of hydrogen peroxide in the solution rapidly decreases; further, the solution gradually loses in total active oxygen, but the loss in hydrogen peroxide is much greater than the loss in total active oxygen.

(3) At each interval the total active oxygen present as peroxide and peracid is considerably greater than that originally present as peroxide. Acetic peracid is, therefore, formed

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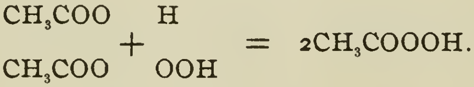
[1] Clover and Richmond: *Loc. cit.*

at the expense of the active oxygen of the hydrogen peroxide.

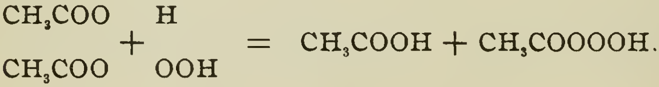
The solution of hydrogen peroxide employed contained a small amount of soluble mineral matter, which has a much greater catalytic action upon acetic peracid than upon hydrogen peroxide. This partly accounts for the loss in active oxygen; however, this loss was greatest during the first stages of the reaction at the time when the amount of peracid was smallest. Active evolution of oxygen in the solution was most noticeable during the first hour or two. The greater part of the loss is, therefore, intimately connected with the reaction itself. During the last stages of the reaction the peracid is evidently decomposed faster than it is formed.

The action of hydrogen peroxide upon acetic peroxide resulting in the formation of more peracid than would be formed by the ordinary hydrolysis, is most easily explained as follows:



$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix} + \begin{matrix}H\\OOH\end{matrix} = 2CH_3COOOH.$$

Owing to the instability of the substances in question it is not possible to say that they react in the proportion indicated. The reaction suggests that of water upon acetic peroxide. Looked on in this light the possibility of a reaction, according to the following equation, suggests itself:



$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix} + \begin{matrix}H\\OOH\end{matrix} = CH_3COOH + CH_3COOOOH.$$

Assuming such a reaction to take place, the loss of oxygen, already referred to, would be accounted for by the instability of the substance $CH_3COOOOH$, a derivative of the hypothetical trioxide of hydrogen.

A number of experiments, similar to the one described, were carried out with different solutions of hydrogen peroxide, and in all cases the same general results were obtained.

Action of an Aqueous Solution of Hydrogen Peroxide upon Acetic Anhydride.

When acetic anhydride is dissolved in hydrogen peroxide solution both acetic peracid and peroxide are soon present in the solution. The peracid in the solution may result from the hydrolysis of previously formed peroxide, or it may be formed directly by the action of hydrogen peroxide upon anhydride. A study of the rates of formation of these two substances has led to the conclusion that the peracid is the first substance formed.

The rate of formation of peracid in solutions of hydrogen peroxide of different strength is shown in the table given below. The best commercial hydrogen peroxide was used, which was concentrated to the strength given by distillation in a vacuum. The acetic anhydride was fractionated before using.

Twenty cc. of hydrogen peroxide solution (61.6 grams per liter) were brought to a temperature of 21° and 1 cc. of acetic anhydride added. The latter was dissolved quickly by shaking and the solution was kept at 21°. At different intervals, 1 cc. of the resulting solution was removed and the peracid present estimated in the manner already described. As the intervals of time are necessarily small, on account of the rapidity of the reaction, it was necessary to fill the pipette just before the time indicated and at the proper time to deliver the solution into a large volume of water, in order to stop or greatly retard any further reaction between the constituents. The results obtained appear in the first column below. In the second column are the results of a duplicate experiment carried out in exactly the same manner.

A solution of hydrogen peroxide of different strength (45.4 grams per liter) was also employed. The experiments with this solution were carried out in exactly the same way as described above, all conditions and measurements being the same. The results duplicated are placed in columns III. and IV.

Time in minutes.	I. N/20 thiosulphate.	II. N/20 thiosulphate.	III. N/20 thiosulphate.	IV. N/20 thiosulphate.
3	1.0	1.0	0.7	0.75
6	1.4	1.3	0.9	0.9
9	1.6	1.5	1.0	1.0
12	1.7	1.65	1.1	1.1
15	1.8	1.75	1.2	1.2
18	1.9	1.95		
21		2.2		
27		2.5		
30		2.6		

It will be noted that the rate of formation of peracid is large at first, but is soon checked. So long as acetic anhydride is present in the solution there would be a limit to the concentration of peracid owing to the ready reaction between the two substances.[1]

As soon as anhydride is removed from the solution, the formation of peracid by the hydrolysis of peroxide should continue at a uniform rate. To determine whether or not the relatively large amounts of peracid present in the solution at the earlier intervals can be accounted for by the hydrolysis of peroxide present, necessitates a determination of the amount of the latter substance in the solution at different intervals.

The amount of acetic peroxide was obtained as in the previous case, by subtracting from the total active oxygen the sum of the active oxygen as hydrogen peroxide and as peracid. The total active oxygen was obtained in the manner already described. The hydrogen peroxide was also estimated as previously described. Careful experiments showed that a known amount of hydrogen peroxide could be accurately estimated under the conditions employed and in the presence of the maximum amount of peracid, peroxide, and anhydride which might be in the solution to be examined. As this determination is of vital consequence to the results obtained and the conclusions drawn, a few of these experiments will be given.

A definite volume of hydrogen peroxide solution was estimated in the usual manner with N/20 permanganate. Required, 16.8 cc.; duplicated, 16.85 cc.

[1] Clover and Richmond: *Loc. cit.*

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2N) and again estimated. Required, 16.85 cc.; duplicated, 16.85 cc.

The same volume of hydrogen peroxide was added to 250 cc. of dilute sulphuric acid (2N). 0.05 gram of acetic anhydride was added, together with a solution of acetic peroxide, which had stood four or five hours and was equivalent to 4 cc. N/20 thiosulphate "immediate," and 9 cc. total. Required, 16.85 cc. permanganate.

The estimation of acetic peroxide in this manner is dependent upon three other determinations, each of which is liable to a reasonable experimental error. The numbers obtained are, therefore, approximate ones, but are all that can be desired.

The following experiments were made with the same solutions of hydrogen peroxide as were previously employed in the estimation of peracid, and were carried out in exactly the same manner, care being taken to make all conditions and measurements the same. The portion to be estimated for hydrogen peroxide was delivered into 500 cc. of water at the proper time. Only a portion of this was titrated, the numbers appearing in the table representing the entire amount. It was not necessary to remove the portion to be estimated for total active oxygen at exactly the time indicated, as there is little variation in this value, during the time of the experiment. The figures in the table represent the amounts of N/20 solutions required by 1 cc. of the reaction mixture:

Hydrogen Peroxide, 61.6 Grams Per Liter.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate	Thiosulphate representing peroxide.
3	68.7	1.0	66.95	0.75
6	68.8	1.35	66.1	1.35
18	68.7	1.9	64.4	2.4
30	68.9	2.6	64.2	2.1

Hydrogen Peroxide, 45.4 Grams Per Liter.

Time in minutes.	Total thiosulphate.	Immediate thiosulphate.	Permanganate.	Thiosulphate representing peroxide.
3	51.0	0.7	49.9	0.4
6	50.8	0.9	48.1	1.8
18	50.8	1.3	46.65	2.85

Repetition of these experiments a number of times gave values which varied within a comparatively narrow range for reasons already mentioned. In no case, however, were the numbers found to exceed those given by more than 1.0.

Experiments were made to determine the rate of hydrolysis of acetic peroxide in a solution of hydrogen peroxide. The solutions of hydrogen peroxide used were the same as in the previous experiments. A solution of acetic peroxide (approximately N/5) was made by dissolving 1.2 grams of pure acetic peroxide in 100 cc. of hydrogen peroxide. This concentration of acetic peroxide is considerably greater than that at any time in either of the solutions examined. The temperature remained at 21°. The peracid in 1 cc. of the solution was estimated at intervals in the usual manner. The amount is represented in the tables below by N/20 thiosulphate, column I. representing the stronger solution of hydrogen peroxide and column II. the weaker:

Time in minutes.	I.	II.
2	0.2	0.2
4	0.3	0.3
8	0.45	0.4
16	0.8	0.6

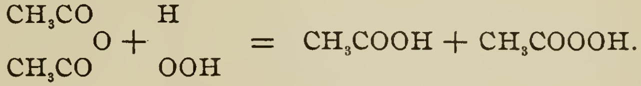
These numbers are to be compared with those obtained for peracid in the previous experiments. It is evidently impossible to account for the amount of peracid in those solutions, assuming that it is formed by the hydrolysis of acetic peroxide. The comparison applies especially to the earlier stages of the reaction. It is known that later acetic peroxide is formed in considerable amount, and that this eventually hydrolyzes to peracid.

To make sure that the acetic acid present in the original experiment had no accelerating action on the rate of hydrolysis of the peracid, the reactions were compared in hydrogen peroxide solution of about 5.5 per cent, and in a 10 per cent acetic acid solution, containing the same concentration of hydrogen peroxide. The same amount of pure acetic peroxide was added to each solution. The amounts of peracid formed at intervals in 1 cc. of the solutions as represented by N/20 thiosulphate are given below:

Time in minutes.	Acetic acid solution.	Unacidified solution.
20	0.3	1.1
40	0.6	1.8
60	0.8	2.3

It will be seen that the acid has a retarding rather than an accelerating influence.

It is evident that acetic peracid results directly from the action of acetic anhydride upon hydrogen peroxide, probably according to the following equation:



$$\left.\begin{matrix}CH_3CO\\ CH_3CO\end{matrix}\right. O + \begin{matrix}H\\ OOH\end{matrix} = CH_3COOH + CH_3COOOH.$$

This reaction is analogous to that of acetic peroxide upon hydrogen peroxide, already considered. Here again, we must notice the similarity between the action of hydrogen peroxide and ordinary hydrolysis by means of water.

One of us has previously shown[1] that peracids, even in very dilute solutions, are extremely reactive toward substances capable of ordinary hydrolysis. It was shown that either benzoic or acetic peracids could be almost completely converted into benzoic acetic and acetic peroxides, respectively, even in very dilute aqueous solution, by the addition of a small amount of acetic anhydride to the solution. The formation of the peroxide is, therefore, to be explained by the action of peracid upon unchanged anhydride. The great tendency for these substances to react is seen in the sudden check in the rate of formation of peracid during the reaction of acetic anhydride upon the solution of hydrogen peroxide.

Propionic anhydride was also found to show the same general behavior toward hydrogen peroxide as acetic anhydride. Its action is slower, but on account of its sparing solubility it is less suitable for study.

Since acetic peroxide is almost completely changed to peracid in the course of twenty-four hours, experiments were made to determine the practicability of preparing a solution of acetic peracid by allowing a solution of anhydride in hydrogen peroxide to stand for this length of time.

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[1] *Loc. cit.*

(1) Two cc. of acetic anhydride were added to 100 cc. of a 3.2 per cent commercial hydrogen peroxide solution, and kept cool by immersing in a vessel of water. After twenty-four hours the total amount of peracid in the solution estimated in the usual manner was 0.33 gram. From this it follows that about 22 per cent of the anhydride entered into reaction with hydrogen peroxide.

(2) Five cc. of acetic anhydride were added to 100 cc. of the same hydrogen peroxide solution and kept cool. After twenty-four hours the solution contained 0.82 gram peracid. Here again, 22 per cent of the anhydride entered into combination with the hydrogen peroxide.

(3) Ten cc. of anhydride were added to 100 cc. of the same hydrogen peroxide solution, and kept cool. After twenty-four hours there were 1.54 grams of peracid in the solution. In this case 21 per cent of the anhydride entered into reaction with the hydrogen peroxide.

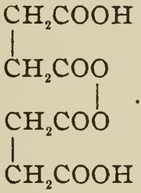
These experiments bring out an important fact ; namely, that the rate of the reaction of hydrogen peroxide with anhydride is much greater than that of water with anhydride. From the relative concentrations of the two substances in the above solutions it might be expected that if the rates were nearly equal, only a little over 3 per cent of the anhydride would have reacted with the hydrogen peroxide. The fact that about the same per cent was obtained in the three experiments shows that the acetic acid has little influence upon the relative rates. An excess of hydrogen peroxide was present in each experiment. In the third only a little over 20 per cent of the hydrogen peroxide was used, and in the others much less. The secondary reaction of anhydride upon peracid would only tend to destroy the anhydride, and decrease the yield of peracid, as the active oxygen remains the same after this reaction.

A much better yield of peracid may be obtained by using a stronger solution of hydrogen peroxide, easily obtained by concentrating in a vacuum.

Twenty cc. of a solution of hydrogen peroxide containing 104 grams per liter were added to 6.1 grams of anhydride, and the mixture shaken and kept cool until the anhydride had gone into solution. It was then allowed to stand in a vessel of water for twenty-four hours. At the end of this time hydrolysis was complete, and the solution contained about 2 grams of peracid, about 45 per cent of the theoretical yield.

Anhydrides of Dibasic Acids.

Succinic Peroxide Acid,



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \qquad\quad | \\ CH_2COO \\ | \\ CH_2COOH \end{array}$$

.—When a 3 per cent solution of hydrogen peroxide is saturated with succinic anhydride, the oxidizing power of the solution rapidly changes, as can be noted by its effect on potassium iodide. The products of the reaction remain dissolved, however, as there is no precipitation from the solution. If a stronger solution of hydrogen peroxide be employed and excess of anhydride be added, and the mixture shaken, so as to keep the solution saturated with the anhydride, a precipitation soon occurs. The anhydride used was in the form of broken pieces of a solid product, and after agitation it quickly settled to the bottom of the vessel. The precipitate consists of very fine crystals, and remains suspended in the liquid. After a considerable quantity had formed it was filtered, washed several times with water, dried quickly by packing tightly on a porous plate, then pulverized and allowed to remain in a vacuum for several hours. For analysis it was recrystallized from acetone. The active oxygen was estimated by dissolving the substance in a small amount of water, adding an excess of potassium iodide, and titrating at once with standard thiosulphate.

0.2383 gram substance gave 0.3563 gram CO_2 and 0.0871 gram H_2O.

0.1232 gram substance required 20.82 cc. N/20 thiosulphate.

	Calculated for $C_8H_{10}O_8$.	Found.
C	41.00	40.78
H	4.31	4.10
O (Active)	6.84	6.78

The amount of succinic acid present in the substance after complete hydrolysis and removal of active oxygen was determined and found to agree with the theoretical.

The substance was covered with about 20 parts of water in a test-tube, a pinch of platinum black added, and allowed to stand for a week. The succinic acid formed was then estimated by titrating with N/10 potassium hydroxide.

0.1954 gram substance required 33.25 cc. N/10 KOH.

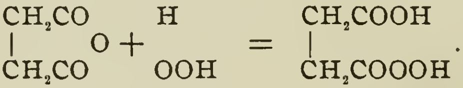
Calculated, 33.40 cc.

0.1290 gram substance required 22 cc. N/10 KOH.

Calculated, 22.05 cc.

The substance is moderately soluble in water, alcohol, acetone, and acetic ether; sparingly in ether; insoluble in chloroform, benzene, and ligroin. It is colorless and, when pure, odorless. The crystals are flat plates, generally very irregular. The substance begins to soften at 115° and is completely melted at 128° with decomposition. When brought into a flame it explodes; it does not explode on percussion or friction. When openly exposed to the air it slowly deteriorates, but when well stoppered no deterioration could be detected after several months.

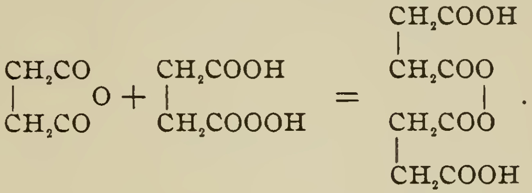
Assuming the action of succinic anhydride upon hydrogen peroxide to be similar to that of acetic anhydride, the first step is the formation of succinic monoperacid,



$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} O + \begin{array}{l} H \\ \\ OOH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array}.$$

At the same time a certain amount of anhydride undergoes ordinary hydrolysis with water with the formation of succinic acid. The strength of the hydrogen peroxide solution employed determines the proportion in which the anhydride enters into each of these reactions. Succinic monoperacid is very soluble in water and does not separate from the solution.

The second step in the formation of the peroxide acid is the action of succinic monoperacid upon succinic anhydride :



$$\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}O + \begin{array}{l}CH_2COOH\\ |\\ CH_2COOOH\end{array} = \begin{array}{l}CH_2COOH\\ |\\ CH_2COO\\ \qquad|\\ CH_2COO\\ |\\ CH_2COOH\end{array}.$$

The best yield of the peroxide acid is obtained by employing a 7.5 to 8 per cent solution of hydrogen peroxide.

Ten grams of ordinary crystalline succinic anhydride were added to 25 cc. of 7.5 per cent hydrogen peroxide and the mixture shaken. The temperature gradually rose, but was kept below 30°. At the end of thirty-five minutes there was no further rise in temperature, indicating that all anhydride had been dissolved. The product was then filtered and washed several times with small portions of water. It was then packed tightly on a porous plate, placed in a warm place, and after an hour was perfectly dry. An analysis showed the substance to be pure. Yield, 7.5 grams.

When excess of the peroxide is added to water and shaken the amount dissolved gradually increases. This increase is due to the hydrolysis of the dissolved peroxide, which takes place according to the laws previously developed.[1] The rate of the reaction is much greater than that with any peroxide previously studied.

An excess of finely pulverized peroxide was continuously shaken with water at about 24°. At intervals of five, ten, fifteen, and twenty-five minutes a small portion of the mixture was filtered and the amount of peroxide dissolved was determined. At the end of five minutes the solution contained 19.8 grams per liter ; at the end of ten minutes, 24.5 grams per liter ; at the end of fifteen minutes, 28.4 grams per liter ; and at the end of twenty-five minutes, 35.8 grams per liter. At this rate of hydrolysis, the original solubility may be placed approximately at 15 grams per liter. At the end of fifteen minutes the original solubility is almost doubled.

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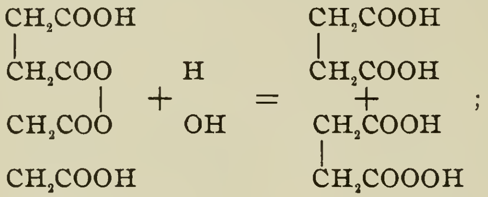
[1] *Loc. cit.*

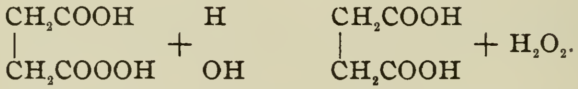
A large excess of peroxide was added to water in a beaker and kept stirred continuously for several hours. The rate of hydrolysis as indicated by the active oxygen content of the solution was found to decrease as the solution became stronger. At the end of one-half hour hydrogen peroxide could easily be detected in the solution by means of the titanic or chromic acid tests. After six hours an appreciable portion of the active oxygen of the solution (over 0.5 per cent) was present as hydrogen peroxide. By this means it was possible to obtain a very strong solution of the products of hydrolysis. The substance hydrolyzes according to the following equations. The second change is much slower than the first :

(1)



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \qquad\;\; | \\ CH_2COO \\ \\ CH_2COOH \end{array} + \begin{array}{l} H \\ OH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \\ \quad + \\ CH_2COOH \\ | \\ CH_2COOOH \end{array} ;$$

(2)



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOOH \end{array} + \begin{array}{l} H \\ OH \end{array} \quad \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} + H_2O_2.$$

Succinic peroxide acid presents a striking difference from other bodies of the peroxide type in the behavior af the unhydrolyzed substance toward potassium iodide. The action of the peroxide, as well as its hydrolytic product upon potassium iodide, is almost immediate, so that the substances cannot be distinguished from each other as could the peroxides and peracids of monobasic acids. When an excess of potassium iodide is added to a fresh saturated solution of the peroxide acid, or to the same solution after standing an hour, and which would, therefore, be mostly hydrolyzed, the calculated amount of iodine is liberated in the short time required to make the titration with standard thiosulphate. If the solution is very dilute, a minute or two is required before the liberation of iodine is complete. It was not possible, therefore, to study the hydrolysis of the peroxide acid in dilute solution. The change into hydrogen peroxide could be followed, however, by comparing the immediate liberation of iodine with the total.

The following figures indicate the gradual formation of hydrogen peroxide : (1) in a 1 to 1000 solution, and (2) in a 1 to 100 solution :

Time in days.	(1) Per cent of active oxygen as H_2O_2.	(2) Per cent of active oxygen as H_2O_2.
1	7·3	5·3
2	14.0	8.3
7	41.0	40.0

The active oxygen content of the weaker solution had not appreciably decreased at the end of one week. In the stronger solution there was a decrease of only 1.5 per cent.

In addition to its action on potassium iodide the following are interesting properties, possessed by a solution of succinic peroxide acid. A small amount of manganous salt added to the solution soon produces the deep rose-red color of permanganic acid. The reaction is an extremely delicate test for traces of manganese. The coloration is prevented by the presence of considerable mineral acid. An excess of manganese salt gives, of course, manganese dioxide. The red solution of cobaltous salt is changed to an emerald-green, owing probably to the formation of a cobaltic salt ; the solution slowly evolves oxygen. The addition of sodium acetate to the solution produces a precipitate, probably a higher oxide of cobalt. The green solution of a nickelous salt is soon changed to a purple, which is probably due to the formation of a nickelic salt. The latter seems to be unstable, however, as the solution evolves oxygen and in the course of a few hours the purple color disappears. The addition of sodium acetate to the purple solution causes immediate change to green with evolution of oxygen.

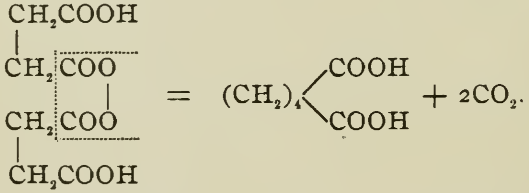
Finely divided manganese dioxide appears to have no catalytic action upon a solution of the peroxide acid, but is oxidized in part to permanganic acid. Lead dioxide has no catalytic action, but platinum black has a slight action. The solution has no effect upon chromic acid, titanic acid, or potassium permanganate, until it has stood an hour or more and hydrogen peroxide has been formed.

As already stated, succinic peroxide acid, like all peroxides, decomposes when heated. The decomposition was studied by adding the substance to xylene, which was heated to its boiling-point. Carbon dioxide was evolved, the amount being a little less than 1 molecule per molecule of peroxide. Only a trace, if any, of oxygen or hydrocarbons was evolved. On cooling the xylene a crystalline product separated, which was about 50 per cent of the original weight of substance. This product consisted chiefly of succinic anhydride, which was removed by digesting with chloroform on the water-bath. The residue was distilled, whereupon water, succinic acid, and anhydride passed over. The residue from this distillation consisted chiefly of adipic acid, which was recrystallized from water and identified by its melting-point.

0.1204 gram substance required 16.45 cc. N/10 KOH.

Calculated for adipic acid, 16.45 cc.

From the original xylol solution there was obtained, after removal of the solvent, a gummy residue, which dissolved completely in sodium carbonate. It was not identified. A small portion of the substance, therefore, decomposes as follows:



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COO \\ \qquad\;\; | \\ CH_2COO \\ | \\ CH_2COOH \end{array} = (CH_2)_4\left\langle\begin{array}{l} COOH \\ COOH \end{array}\right. + 2CO_2.$$

The major portion, however, decomposes to yield succinic anhydride, and the gummy acid substance already mentioned.

Vanino and Thiele[1] have described a substance obtained by the action of succinyl chloride upon sodium peroxide hydrate, which they have called succinyl peroxide and to which they have assigned the formula $C_4H_4O_4$. Baeyer and Villiger[2] have pointed out that the insolubility of the substance in water and in all other solvents renders improbable such a simple formula as the one assigned. We have prepared the substance according to the directions of Vanino and Thiele in order to determine the per cent of active oxygen. There is no way to purify the substance so that the crude product, well washed and dried, was used. This product may be an individual substance or it may be a mixture. The yield obtained was very small. If the substance is covered with a 20 per cent solution of acetic acid and potassium iodide, it gradually goes into solution after six or eight hours, with the liberation of iodine. The percentage of active oxygen, so estimated, was 10.5, a correction having been made for a blank. The percentage calculated for $C_4H_4O_4$ is 13.8. The substance is described in Richter's "Chemie der Kohlenstoff-Verbindungen" as having either the formula

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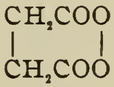
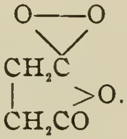
[1] Ber. d. chem. Ges., **29**, 1724.

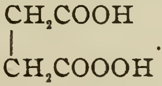
[2] *Ibid.*, **34**, 762.



or



There is certainly no ground at present for assigning any formula to the substance, even assuming that the product in question is homogeneous in composition.

Succinic Monoperacid,  $\begin{array}{l}CH_2COOH\\ |\\ CH_2COOOH\end{array}$.—Ten grams of succinic peroxide acid were covered with about 75 cc. water in a beaker and stirred continuously at a temperature of about 30°. At the end of three or four hours the entire amount had gone into solution. It was then removed to an evaporating-dish and allowed to remain in a vacuum over night with sulphuric acid. The dry residue consisted of about 45 per cent of succinic monoperacid. The monoperacid is more soluble in chloroform than succinic acid, and may be removed from the latter by digesting the mixture with chloroform at 50°, filtering, and cooling the solution. In this way the substance is obtained fairly pure. It may be recrystallized from a mixture of chloroform and ether, from which it separates in large crystals on standing. The percentage of active oxygen contained by various samples which were recrystallized several times, varied from 10.5 to 11.3, while the theoretical is 11.9. This deficiency may have been due to the fact that when the substance is dissolved in water a decided evolution of oxygen is noticeable; it was necessary to dissolve in water to estimate the active oxygen. A sample recrystallized twice contained 11 per cent of active oxygen and when rapidly heated melted at 107° with decomposition.

0.1170 gram substance gave 0.1546 gram CO_2 and 0.0473 gram H_2O.

	Calculated for $C_4H_6O_5$.	Found.
C	35.81	36.03
H	4.52	4.53

The substance is much more soluble in water than succinic acid. The same relation exists between the solubilities of benzoic acid and peracid. It also dissolves freely in alcohol, acetone, and acetic ether. It is only moderately soluble in ether and sparingly in chloroform. It has very little, if any, odor and does not, in the least, remind one of hypochlorous acid, as do benzoic and acetic peracids. It gradually decomposes on standing, but is more stable than benzoic peracid. A sample consisting of a mixture of succinic acid and monoperacid was found on analysis to consist of 60 per cent of the latter. After standing for a week in a stoppered vessel the percentage of monoperacid was only 55.4.

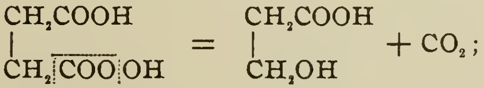
When a strong aqueous solution of the substance (either pure or mixed with succinic acid) is saturated with succinic anhydride, a heavy precipitate of succinic peroxide acid soon appears; more quickly on cooling and scratching with a glass rod. When glutaric anhydride is dissolved in a strong solution of the monoperacid the mixed peroxide acid of succinic and glutaric acids is formed and on cooling separates from the solution. This substance will be described later.

The decomposition of succinic monoperacid is interesting. The mixture of acid and monoperacid was used for this study.

It was mixed with infusorial earth in order to moderate the action.

Three and five-tenths grams of the mixed acids containing 1.6 grams of monoperacid were mixed with 5 grams of infusorial earth and placed in a small flask connected with a carbon dioxide generator and a gasometer. The air in the flask was completely replaced by carbon dioxide and the flask was then slowly heated in an oil-bath, and the gas evolved was collected over water in the gasometer. The volume of gas evolved was about 350 cc. This consisted almost entirely of carbon dioxide, with only a trace of oxygen and a small amount (about 3 per cent) of a combustible gas. The amount of carbon dioxide obtained is a little in excess of 1 molecule from 1 molecule of the monoperacid.

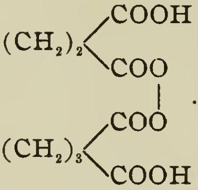
The experiment was repeated in order to determine the nature of the non-gaseous products. After the decomposition was completed the contents of the flask were distilled. Considerable water passed over at first and the temperature gradually rose to 140°. The distillate possessed the characteristic odor of acrylic acid. That it consisted in a large part of this substance was shown by treating it with concentrated hydriodic acid, whereupon β-iodopropionic acid crystallized from the solution. This was recrystallized from water and identified by its melting-point. The decomposition may be explained as follows:

(1) 

$$(1)\quad \begin{array}{l} CH_2COOH \\ | \\ CH_2\vdots\overline{COO}\vdots OH \end{array} = \begin{array}{l} CH_2COOH \\ | \\ CH_2OH \end{array} + CO_2;$$

$$(2)\quad CH_2OHCH_2COOH = CH_2{=}CHCOOH + H_2O.$$

The substance first splits off carbon dioxide. The β-hydroxypropionic acid, which is probably formed as an intermediate product, then splits off water with the formation of acrylic acid. The decomposition probably takes place almost entirely in the manner indicated. Baeyer found that benzoic peracid decomposed with the formation of benzoic acid and oxygen. The results obtained with succinic monoperacid have suggested that possibly phenol is also formed during the decomposition of benzoic peracid. This is made probable from the fact that benzoic peracid becomes colored on standing. Phthalic monoperacid, discovered and described by Baeyer, was found to yield salicylic acid on decomposition. This was identified by its color test with ferric chloride.



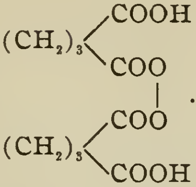
Succinic Glutaric Peroxide Acid, .—Ten cc. of a solution of succinic monoperacid containing 1.47 grams of this substance and which was free from hydrogen peroxide was treated with 1.5 grams of glutaric anhydride. The latter substance was dissolved after shaking for a minute. The solution was kept cool under a tap and after about five minutes a crystalline precipitate appeared. After standing for five minutes longer the product was filtered, washed several times with small portions of water, and packed tightly on a porous plate. When dry, the substance was practically pure. Yield, 1.2 grams. For analysis it was recrystallized from a mixture of ether and acetic ether.

0.0825 gram substance required 13.25 cc. N/20 thiosulphate.

0.1473 gram substance gave 0.2344 gram CO_2 and 0.0650 gram H_2O.

	Calculated for $C_9H_{12}O_8$.	Found.
C	43.52	43.40
H	4.88	4.96
O (Active)	6.45	6.40

The substance begins to soften at 105° and melts at 107° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether, and sparingly soluble in ether. The crystals are similar in appearance to those of succinic peroxide acid. When potassium iodide is added to a saturated solution of the substance, it must stand two or three minutes before the theoretical amount of iodine is liberated. In oxidizing action it is, therefore, less powerful than succinic peroxide acid.

Glutaric Peroxide Acid,  .—Three grams of glutaric anhydride were dissolved in 6 cc. of 8 per cent hydrogen peroxide. The solution was kept cool and the peroxide acid soon crystallized out. After twelve minutes it was filtered off, washed well with small portions of water, and dried on a porous plate. The dried substance was practically pure. Yield, 1.9 grams. For analysis it was crystallized from acetic ether.

0.0888 gram substance required 13.25 cc. N/20 thiosulphate.

0.1578 gram substance gave 0.2640 gram CO_2 and 0.0756 gram H_2O.

	Calculated for $C_{10}H_{14}O_8$.	Found.
C	45.77	45.61
H	5.39	5.37
O (Active)	6.10	5.97

The substance melts sharply at 108° with decomposition. It is quite soluble in alcohol, acetone, and acetic ether; moderately soluble in ether; and very sparingly in chloroform and benzene. The substance hydrolyzes in aqueous solution and the solubility and rate of hydrolysis were determined at 24° in the same manner as with succinic peroxide acid.

The amounts of peroxide acid contained in 1 liter of solution at intervals of five, ten, fifteen, and twenty-five minutes were 9.75, 10.75, 11.6, and 13.75 grams, respectively. At this rate of hydrolysis the original solubility may be placed approximately at 8.75 grams per liter.

The action of glutaric peroxide acid upon potassium iodide is markedly different from that of succinic peroxide acid. The action is very slow, like that of hydrogen peroxide. As in the case of the latter substance, the time required for the complete liberation of iodine is greatly decreased by the addition of dilute sulphuric acid. Except in very dilute solution of peroxide the theoretical amount of iodine is liberated in fifteen minutes when excess of potassium iodide has been added.

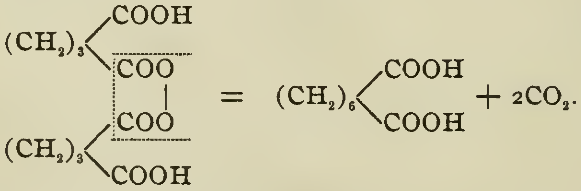
The decomposition of glutaric peroxide acid was studied in the same manner as that of the succinic compound.

Four and five-tenths grams of the substance were added in small portions to 15 cc. of boiling xylene. The non-volatile products of decomposition remained dissolved, but, on cooling, 0.6 gram of colorless crystals was deposited. This product was found to be almost pure suberic acid. The substance was purified by recrystallizing from water and melted at 140° (suberic acid 140°).

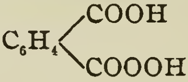
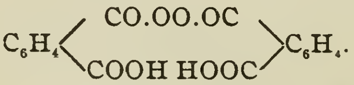
0.1156 gram substance required 13.45 N/10 KOH.

Calculated, 13.3 cc.

On distilling off the xylene from the filtrate previously mentioned, a fatty residue remained which was soluble in sodium carbonate. The decomposition takes place only to a certain extent as follows:



$$\begin{array}{l}(\mathrm{CH_2})_3\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{COO}\end{array}\right.\\ \qquad\qquad\quad | \\ (\mathrm{CH_2})_3\left\langle\begin{array}{l}\mathrm{COO}\\ \mathrm{COOH}\end{array}\right.\end{array} = (\mathrm{CH_2})_6\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}\right. + 2\mathrm{CO_2}.$$

By the action of sodium hydroxide and hydrogen peroxide upon phthalic anhydride, Baeyer and Villiger[1] have isolated phthalic monoperacid,  $\mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOOH}\end{array}\right.$, and phthalic peroxide acid,  $\mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO.OO.OC}\\ \mathrm{COOH\ HOOC}\end{array}\right\rangle\mathrm{C_6H_4}$.

These authors have offered no explanation of the reactions involved. If we consider that the addition of an alkali to a solution of hydrogen peroxide results in the formation of a salt of this substance, either MOOH or MOOM, then the reaction between such a solution and an anhydride may be looked upon as follows :

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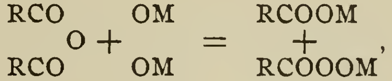
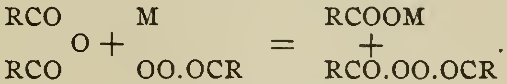
[1] Ber. d. chem. Ges., 34, 762.

(1) 

$$\begin{matrix} \mathrm{RCO} & & \mathrm{OM} & & \mathrm{RCOOM} \\ & \mathrm{O} + & & = & + \\ \mathrm{RCO} & & \mathrm{OM} & & \mathrm{RCOOOM} \end{matrix},$$

and (2) 

$$\begin{matrix} \mathrm{RCO} & & \mathrm{M} & & \mathrm{RCOOM} \\ & \mathrm{O} + & & = & + \\ \mathrm{RCO} & & \mathrm{OO.OCR} & & \mathrm{RCO.OO.OCR} \end{matrix}.$$

Such a view would explain all of the reactions which are known to take place between sodium peroxide, barium peroxide, etc., and acid anhydrides, chlorides, etc. This explanation is, however, not in accord with the views of Calvert,[1] who, after attacking from all sides the problem of the condition of hydrogen peroxide in alkaline solution, arrived at the conclusion that a compound of the type MO_2 is formed, M being a univalent metal. The work of Calvert has certainly shown that 1 molecule of alkali is capable of holding in combination more than 1 molecule of hydrogen peroxide. This behavior might be due to the formation of an addition-compound between hydrogen peroxide and its primary salt, such as KHO_2,H_2O_2. Schöne[2] has isolated compounds of this type by evaporating an alkaline solution of hydrogen peroxide in a vacuum. A compound[3] containing sodium acetate and hydrogen peroxide crystallizes out on adding sodium peroxide to acetic acid. Tanatar[4] has isolated compounds between other salts and hydrogen peroxide. Calvert showed that the solubility of potassium chlorate is greater in a solution of hydrogen peroxide than in water, and that its electric conductivity is less, although it would be expected to be greater, on account of the dielectric constant of hydrogen peroxide being greater than that of water. Jones and Carroll[5] further found that the depression of the freezing-point, brought about by various salts in hydrogen peroxide solution, was less than that in water, and have pointed out the probability that compounds are formed between hydrogen peroxide and salts in solution. An unstable compound between the benzoylated hydrogen peroxide and its sodium salt has been observed by Baeyer and Villiger.[1] A number of weak acids are known to form compounds of this type, and we may even look at compounds containing water of crystallization in the same light. It is not known whether or not such compounds are completely dissociated in aqueous solution. The similarity between hydrogen peroxide and water which has been pointed out in this article makes it appear possible that water enters into combination with neutral salts dissolved in it. In this connection the results obtained by Calvert and by Jones and Carroll appear especially interesting.

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[1] Ztschr. phys. Chem., **38**, 513.

[2] Ann. Chem. (Liebig), **193**, 241.

[3] Tafel : Ber. d. chem. Ges., **27**, 816.

[4] Ztschr. anorg. Chem., **28**, 255.

[5] This JOURNAL, **28**, 284.

The following may be summed up as the chief reactions which are known to take place when an anhydride is dissolved in an aqueous solution of hydrogen peroxide :

(1) Ordinary hydrolysis with water.

(2) Analogous reaction with hydrogen peroxide resulting in the formation of a peracid.

(3) Action of peracid on anhydride with the formation of an acid peroxide.

(4) Ordinary hydrolysis of peroxide with water.

(5) Action of hydrogen peroxide upon acid peroxide with the formation of 2 molecules of peracid and also with loss of oxygen, possibly due to the intermediary formation of a derivative of hydrogen trioxide.

(6) Slow hydrolysis of peracid to acid and hydrogen peroxide.

(7) Slow decomposition of both peracid and hydrogen peroxide with evolution of oxygen.

LABORATORY OF GENERAL CHEMISTRY,
UNIVERSITY OF MICHIGAN,
ANN ARBOR, Feb. 13, 1904.

[1] Ber. d. chem. Ges., 33, 1569.

ON INULIN.

By Arthur L. Dean.

Numerous investigators have undertaken the study of inulin, some approaching their work with the aim and equipment of the botanist, some with those of the chemist. In general, the chemical investigations have contributed in a marked degree to the clearer understanding of the physiological rôle of inulin in plants. In the course of certain investigations on the physiological relations of inulin I have been led to study its behavior as a chemical compound with results which seem worth recording.

From the researches of the older workers the methods of preparation and the properties of inulin were fairly well established. In order to obtain preparations of inulin, the tissues containing it—almost always the underground parts of *Inula Helenium*, *Helianthus tuberosus*, or *Dahlia variabilis*—are finely divided, the juice squeezed out. the residue boiled with water with the addition of a little calcium carbonate to neutralize any acidity, and the fluid pressed out. The juice and the extract are united, purified with lead acetate, the excess of lead removed with hydrogen sulphide, and the filtrate from the lead sulphide neutralized with ammonia or calcium carbonate. The inulin in this solution, after concentration to a small volume, is removed either by freezing or by adding alcohol until the fluid contains about 60 per cent thereof. The product obtained in this manner is frequently somewhat discolored and sometimes contains traces of sugar. It may be purified by redissolving it in hot water, filtering through animal charcoal, and again precipitating by alcohol or freezing. The inulin obtained in this way is a white, odorless, tasteless solid, very sparingly soluble in cold water, readily soluble in hot water, and practically insoluble in cold alcohol of 60 per cent strength or over. It does not reduce Fehling's solution, but on short boiling with acids or by the action of the enzyme inulase this carbohydrate is hydrolyzed to levulose, which readily reduces Fehling's solution. The well-known Seliwanoff's reaction[1] is given brilliantly. Inulin is optically active, turning the plane of polarized light to the left. The exact amount of its specific rotation has been variously given, but in general the figures have ranged from $[\alpha]_D = -33°$ to $-40°$.

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[1] On boiling solutions of the ketones, or their polymers, with 18 per cent of hydrochloric acid and a little resorcinol, a brilliant cherry-red color is produced with the subsequent separation of a red precipitate.

As stated above, the ordinary sources of inulin are the fleshy underground organs of the elecampane, artichoke, and dahlia. Preparations have also been made from chicory and dandelion roots. On account of the fact that in pieces of these plant organs kept in alcohol, sphaerocrystals of inulin develop, this reaction has been used as a microchemical test for inulin. Using this method, various investigators have tested a considerable range of plant species for the presence of this carbohydrate. Foremost among these researches should be mentioned those of G. Kraus, who showed that besides the wide occurrence of inulin in reserve places—outside the seeds—in the *Compositæ*, it is also present in members of the *Campanulaceæ*, *Lobeliaceæ*, *Goodeniaceæ*, and *Stylideæ*.[1] Kraus also made preparations of inulin from several of these non-composites and established its similarity, if not its identity, with the inulin of the *Compositæ*. It was noted by Kraus that glycerol gave this microchemical test as well as, and in some respects better than, alcohol.

Numerous investigators have noted that inulin is accompanied in the *Compositæ* by one or more carbohydrates of somewhat similar nature. Like inulin, they yield levulose on hydrolysis and are more or less insoluble in cold water and alcohol. In general, these compounds stand in an intermediate relation between inulin on the one hand and levulose on the other; they show a lesser laevo-rotation than inulin and a greater solubility. This mixture of substances,—for there can be little doubt that it is a mixture,—has been studied under the various names of levulin, inuloïd, and synanthrose; but the contradictory nature of the results of these studies of the levulins leave us with a very hazy knowledge.

The study of the reserve carbohydrates of various other plants, especially members of the monocotyledonous class, has shown that there are here carbohydrates of the same general type as inulin, *i. e.*, they are laevorotary polymers of levulose, more or less insoluble in cold water and alcohol. The following table, although not including all the substances which have been studied, gives some facts about a number of them:

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[1] G. Kraus: Das Inulin-Vorkommen ausserhalb der Compositen. Bot. Zeit., 1877, 329.

Name.	Source.	$[\alpha]_D$.
Irisin	*Iris pseudacorus*	—50 to —54
Sinistrin	*Scilla maritima*	—44 to —48
Graminin	*Trisetum alpestre et al.*	—38.9
Phlein	*Phleum pratense et al.*	—48 to —49

In 1893 there appeared a considerable contribution to our knowledge of inulin and the levulins, embodied in a series of short papers by Tanret.[1] He made the fundamental criticism that all the previous preparations of inulin had been impure, having been contaminated with the levulins, and that therefore the properties of inulin as given by the older workers are incorrect. The new method of preparation, which is described in detail later in this paper, consisted in precipitating the inulin from its solutions as the barium compound by means of barium hydroxide. This barium compound, on account of its greater insolubility, was separated from the barium compounds of the levulins. The levulins, by a further application of the method, were separated from one another, purified, studied, and named. Thus there are, starting from inulin and going down in the series, pseudoinulin, inulenin, helianthenin, and synanthrin. The following table summarizes the more important of Tanret's results:

Aside from the facts outlined in the table, it is noteworthy that Tanret says that on the hydrolysis of inulin he obtained not levulose only, but a mixture of 1 part of dextrose and 12 parts of levulose. The plants experimented with were the artichoke, dahlia, and elecampane, the first named apparently furnishing the bulk of the material worked with.

At the end of Tanret's last paper the following method is given: " Ainsi, étant donné du suc de topinambur, on com-

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[1] "Sur l'inuline et deux principes immédiats nouveaux, la pseudo-inuline et l'inulénine," Compt. rend., 116, 514 (1893); Bull. Soc. Chim., [3], 9, 200: "Sur l'inuline." *bid.*, [3], 9, 227; "Sur les hydrates de carbone du Topinambur," *Ibid.*, [3], 9, 622.

Name.	Form.	$[\alpha]_D$.	Solubility in water at 15° C.	Molecular weight	Formula.[1]
Inulin	Spheroids	—39.5	1 to 10,000	4827	$30(C_{12}H_{10}O_{10})5H_2O_2$
Pseudoinulin	"	—32.2	1 to 350–400	2538	$16(C_{12}H_{10}O_{10})H_2O_2$
Inulenin	Bunches of needles	—29.6	1 to 8	1645	$10(C_{12}H_{10}O_{10})2H_2O_2$
Helianthenin	" " "	—23.5	1 to 1	1924	$12(C_{12}H_{10}O_{10})3H_2O_2$
Synanthrin	Amorphous	Ca —17.0	In all degrees	1319	$8(C_{12}H_{10}O_{10})H_2O_2$

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[1] It should be noted that these formulas are given by an old method whereby the values for carbon and oxygen are twice what they should be; thus the formula of inulin would be written by us as $30(C_6H_{10}O_5)5H_2O$.

mence par le déféquer à chaud par l'extrait de saturne, etc., puis on l'additionne d'un grand excès d'eau de baryte concentrée et on précipite par de l'alcool à 90° et en une seule fois tous les hydrates de carbone. On décompose le précipité par CO_2, on fait bouillir, on filtre, puis on évapore à siccité. Le résidu, traité par l'alcool à 84° bouillant, lui abandonne l'hélianthénine qui se dépose en partie après un repos suffisant, la liqueur n'en retenant que 1/300. Le résidu insoluble est alors traité par l'alcool à 70° bouillant qui enlève l'inulénine. Ce qui reste ne contient plus que la pseudo-inuline et l'inuline, qu'on sépare en les traitant par 10 parties d'alcool à 60° bouillant : la pseudo-inuline y passe et l'inuline reste indissoute."[1] It is stated in the foot-note that inulenin is soluble in 9 parts of boiling 70 per cent alcohol, and insoluble in cold alcohol of that strength; that pseudoinulin is soluble in 6 parts of boiling 60 per cent alcohol, and insoluble in cold; and that inulin is insoluble in cold 60 per cent alcohol and requires 2,000 parts of that strength of boiling alcohol to dissolve it. Tanret adds that he proposes to trace by this method the history of the carbohydrates of the artichoke, but I have been unable to find that he has published anything dealing with these carbohydrates since the appearance of the article quoted from above.

EXPERIMENTAL DATA.

Five plants have served as the sources from which the preparations of inulin to be described have been obtained: *Dahlia variabilis*, *Inula Helenium*, *Helianthus tuberosus*, *Lappa minor*, and a mixture of *Solidago* species. Of these, the first three have long been used as sources of inulin, but, so far as I am aware, no preparations of inulin have been made from the roots of the burdock or from those of the goldenrods. The inulin has been obtained by two methods, the method of the older investigators as described above and by what we will call the second method of Tanret, given in the quotation from the Bulletin of the Chemical Society of Paris.

The fact that the common burdock has long, rather fleshy roots which persist until the time of flowering, suggested the idea that these roots might contain inulin. Accordingly, a number of the roots were dug in October and tested as follows: The roots were washed, grated to a fine pulp, and the mass, together with a little calcium carbonate, was treated with water for about thirty minutes on a boiling water-bath. The fluid was then expressed, lead acetate added in slight excess, the excess of lead removed from the filtrate with hydrogen sulphide, the resulting solution neutralized with ammonia, the fluid concentrated on the water-bath, and treated with an excess of alcohol. After standing over night the precipitate was filtered off, dissolved in water, and the solution run through washed animal charcoal. To this clear, colorless liquid alcohol was added to the strength of 61 per cent. After standing, the precipitate was filtered on a Büchner funnel, washed by being whipped up successively in 60 per cent alcohol, absolute alcohol, and ether, and finally dried. The resulting product was perfectly white, consisted of small spheroids, free from proteid, sparingly soluble in cold water, but readily soluble in hot water. It did not reduce Fehling's solution until after boiling with dilute acids. Seliwanoff's reaction was readily obtained. Dried to constant weight and examined by the polariscope, it was found to be laevorotary, $[\alpha]_D$ being equal to —36°.36. From these properties it is evident that we are dealing with inulin.

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[1] Bull. soc. chim., [3], 9, 629 (1893).

The fibrous roots of the goldenrods present a marked contrast to the fleshy underground parts of the other *Compositæ* which have been examined. Some of these roots, gathered in October and cleaned from gravel as far as possible, were put through the process detailed above and yielded a white preparation consisting of spheroids, giving Seliwanoff's reaction, and reducing Fehling's solution only after boiling with acids. The first preparation, made from the roots of plants still in flower, was noticeably more soluble in cold water than are the ordinary preparations of inulin. A second preparation, made from the roots of plants, the aerial parts of which were already dead, was markedly more insoluble and could not be distinguished by its solubility from the ordinary run of inulin. Examined by the polariscope, this last preparation gave a specific rotation of $[\alpha]_D = -35^\circ.7$. From this evidence it seems safe to conclude that the roots of the goldenrods contain inulin.

I have examined the aerial parts of the inulin-containing plants in a number of instances, and in only one case has evidence of the presence of inulin or of the levulins been obtained. Thus the leaves and stems of the dahlia, the leaves and half-matured seed-heads of the artichoke, the leaves of the goldenrods, and the leaves and petioles of the burdock, all gave negative results. From the stems of the artichoke, however, a preparation was obtained which had the characteristics of inulin except that, like the first preparation from the roots of *Solidago* mentioned above, it was more soluble than inulin in cold water, resembling in this respect a preparation made three days before (October 3rd) from the tubers of an artichoke plant growing near by.

Inasmuch as the older method of preparing inulin gave preparations of inulin possessing differing properties, it seemed advisable to try the method of Tanret to attempt to obtain constant results thereby. The first method given by Tanret, which I have not yet described, was worked through very carefully, as detailed below.

Artichoke tubers gathered partly October 3rd and partly October 17th were ground together, and extracted twice with boiling water with the addition of calcium carbonate. The strained extract was treated with an excess of neutral lead acetate, filtered clear, and sulphuric acid added in very slight excess to remove the excess of lead. The filtrate from the lead sulphate was treated with cold saturated barium hydroxide solution until no more precipitate fell, then 95 per cent alcohol was added until it made one-sixth of the volume of the mixture, then more saturated barium hydroxide solution containing 16 per cent of alcohol until the precipitation was complete. The precipitate was filtered on a Büchner funnel, washed with 16 per cent alcohol saturated with barium hydroxide, then removed from the filter, suspended in water, and decomposed with carbon dioxide, the mixture being warmed during the process to facilitate the reaction. The filtrate from the barium carbonate was cooled and a saturated solution of barium hydroxide added to complete precipitation. This "precipitate (A)" was filtered off and successive small amounts of alcohol added to the filtrate until no more precipitate was obtained. The second precipitate, after removal by filtration, was decomposed with carbon dioxide, the barium carbonate filtered off, and the clear filtrate saved as the "liquid (B)." The "precipitate (A)" was rubbed up in water, decomposed with carbon dioxide, and the filtrate precipitated by barium hydroxide. The filtrate from this new "precipitate (A)" was treated with alcohol and the resulting precipitate decomposed with carbon dioxide, yielding an increment to the "liquid (B)." This process of fractionating (A) was repeated three more times, (A) becoming constantly smaller and the "liquid (B)" constantly increasing. The last time the "precipitate (A)" was smaller than the precipitate resulting from the addition of alcohol to the filtrate from it. Even this very small fraction was not all precipitable by saturated barium hydroxide solution, which is the test by which we are to know that inulin is finally free from admixture with the levulins.

In this experiment, therefore, six successive fractionings of the barium compounds of inulin and the levulins failed to give a separation. No better results followed the attempt to continue Tanret's process on "the liquid (B)" and obtain therefrom pseudoinulin and inulenin.

This rather discouraging result led to a trial of Tanret's second method as given in the quotation from his last paper. Preparations of inulin from all five of the plants named above were made by this method. With one exception the amounts of the various levulins were too small to admit of making polariscopic examinations of them. Their forms, as seen under the microscope, were noted and Fehling's and Seliwanoff's tests were applied. In all cases the precipitates occurring when, according to Tanret, helianthenin and inulenin should have come down, were made up of minute, needle-shaped crystals, generally loosely aggregated into balls. No characteristic difference of form between the two was noted. The precipitates corresponding to pseudoinulin were made up of irregularly sized spheroids and showed a tendency to form a coherent layer at the bottom of the alcohol from which they had separated. The inulin residues remaining after the various extractions with alcohol were more or less discolored and sometimes contained a little insoluble material. They were always dissolved in hot water, filtered, and precipitated by adding alcohol to the strength of 60 per cent. The results of this systematic use of the second Tanret method are given below.

Lappa minor.—Burdock roots, dug November 21st, were cleaned, grated, and put through the second Tanret method. The inulin residue from the alcoholic extractions was so discolored that its solution was run through charcoal before precipitating with alcohol. The precipitate was filtered off and washed with absolute alcohol and ether. Dried to constant weight it showed a specific rotation of $[\alpha]_D = -40^\circ.5$. The precipitates of the levulins were slight.

Inula Helenium.—Roots of the elecampane were dug October 11th. After being comminuted, the material was spread in a thin layer and allowed to dry at laboratory temperature. When air-dry, the tissues were ground to a fine powder and kept in that condition. Tanret's process was applied to an extract obtained by boiling this *Inula* powder with water and a little calcium carbonate. The substance corresponding to the synanthrin of Tanret weighed, air-dry, 3.9 grams. There was no helianthenin precipitate, the inulenin weighed 0.3 gram, the pseudoinulin 0.45 gram, and the inulin, dried to constant weight, 38.6 grams. The specific rotation was equal to $[\alpha]_D = -37^\circ.2$. The preparation contained 0.14 per cent of ash.

Solidago.—The roots of a number of species of *Solidago* were gathered November 15th, washed, and immediately examined for inulin. The precipitates of the levulins were either entirely lacking or very slight. The specific rotation of the inulin obtained was $[\alpha]_D = -37^\circ.2$, which is $1^\circ.5$ higher than the rotation of the inulin obtained by the other method from roots gathered October 24th. The ash of the goldenrod inulin amounted to 0.21 per cent.

Helianthus tuberosus.–Artichoke tubers, dug November 18th, were ground up the same day and an inulin preparation made in the same way as the others. In this case a good yield of helianthenin, 2.1 grams, was obtained. This preparation, which was composed of balls of fine needles, was filtered off, washed with 95 per cent alcohol, absolute alcohol, and ether, and, after drying, examined by the polariscope. It was found to have a specific rotation of $[\alpha]_D = -21°.97$, which is seen to lie between those of Tanret's helianthenin and his synanthrin. Accordingly, this preparation was fractionated to obtain pure helianthenin if possible. Its solution, which was slightly turbid, was shaken up with alumina cream, filtered perfectly clear, and absolute alcohol added to incipient precipitation. After standing over night, the precipitate which had formed was collected on a hardened filter, washed with absolute alcohol and ether, dried, and its specific rotation determined. This was found to be $[\alpha]_D = -26°.06$, which lies midway between helianthenin and inulenin. The preparation of inulin from the artichoke had an ash content of 0.17 per cent and gave a specific rotation of $[\alpha]_D = -33°.4$.

Dahlia variabilis. — Growing plants of the dahlia were rooted up October 29th, and the tuberous roots, after being kept in the laboratory several days, were put through the second Tanret process for inulin. Small quantities of the levulins were obtained and a preparation of inulin having 0.28 per cent of ash and a specific rotation of $[\alpha]_D = -33°.02$. Assuming the correctness of the solubilities given by Tanret and also the specific rotation of inulin given by him, it is remarkable that one should obtain inulin preparations having as low a rotation as those of the inulin of the artichoke and dahlia just described. To further test this point, the inulin obtained from the dahlia was treated with alcohol as follows: Exactly 3 grams of dry inulin were weighed out and boiled twice with 30 cc. of 60 per cent alcohol, made from absolute alcohol by dilution, and the residue was washed on the filter with boiling 60 per cent alcohol. This treatment surely ought to have removed all the levulins if their solubilities are as Tanret gives them. The total alcoholic filtrate and washings were collected in a tared beaker, dried first on the water-bath and finally in the drying-oven, until the residue lost no more weight. This preparation weighed 0.5984 gram and had a specific rotation of $[\alpha]_{\mathrm{D}} = -26^\circ.1$. From this it appears that the undissolved residue weighed 2.4016 grams and had a rotation of $[\alpha]_{\mathrm{D}} = -34^\circ.7$.

Inasmuch as it was thus shown that the second method of Tanret could not be relied upon to give inulin preparations which would always show a specific rotation of 39° to 40°, it was deemed worth while to compare the yields and specific rotations of inulin made by the two methods: that of the older workers which we may call Dragendorff's method and Tanret's second method. Accordingly, some dahlia tubers, which had been taken up in the fall and kept in loam in a cool cellar, were examined in January as follows: The juice of the ground tubers was expressed, the tissue residue boiled in water with a little calcium carbonate, and the fluid expressed. The united extracts were treated with lead acetate n excess and the precipitate removed by filtration. Two portions of this filtrate, of 965 cc. each, were separately worked up for inulin, one by each method. By the Dragendorff method the extract, after removal of the lead with hydrogen sulphide, was percolated through charcoal, concentrated to 140 cc., and precipitated by the addition of absolute alcohol to 60 per cent. The other portion of the extract was treated with a slight excess of sulphuric acid for the removal of the lead, but, on account of the very slight excess of lead acetate, the precipitate of lead sulphate was too small and fine to be removed by filtration. The fluid was accordingly treated with an excess of cold saturated barium hydroxide solution and then methyl alcohol added until it made about 30 per cent of the whole. The copious precipitate was collected in a Büchner funnel, carefully transferred to a beaker, rubbed up with water, and carbon dioxide run in for about one-half hour. Then the mixture was warmed on a water-bath, carbon dioxide being passed in during the warming. The decomposition of the barium inulinate was continued until complete, as shown by the reaction of the fluid and the nature of the precipitate. The solution was boiled, filtered, and the filtrate dried on the water-bath. The residue, which weighed 25 grams (it probably contained much moisture still), was ground to a fine powder and extracted with 250 cc. of 84 per cent alcohol, of 70 per cent alcohol, and of 60 per cent alcohol, respectively, the filtrations being carried out in a hot-water funnel to prevent error by the cooling of the alcohol. The residue was dissolved in 140 cc. of water and precipitated by adding alcohol to 60 per cent. The processes were carried out with great care at every step to avoid losses, although the nature of the processes, especially the Tanret method, precludes very exact quantitative manipulations. Both inulin precipitates were filtered on hardened papers, washed with the same strengths of alcohol, and dried. The inulin by the Dragendorff method was slightly discolored on account of the inadequacy of the charcoal filtration. Dried to constant weight it weighed 22.5 grams and had a specific rotation of $[\alpha]_D = -34°.2$. The inulin by the Tanret method was whiter, weighed 14 grams, and had a rotation of $[\alpha]_D = -36°.8$.

It is worth noticing that the inulin prepared by the Tanret method from *Dahlia*, when the plants were still in vigorous growth, showed a specific rotatory power of $[\alpha]_D = -33°.02$.

It has been observed in many cases that by solution and reprecipitation of inulin preparations the specific rotation rises. Assuming that if such a procedure were repeated until a constant rotation was obtained one would then have pure inulin, the properties of which might be determined, I carried out the experiments to be detailed.

I. Preparation A ; from Lappa minor.—A1. Prepared from burdock by Dragendorff's method. $[\alpha]_D = -35°.3$.

A2. A1 dissolved, precipitated by alcohol to 60 per cent, washed in cold 60 per cent, and boiled in 60 per cent alcohol. $[\alpha]_D = -37°.6$.

A3. A2 treated as last. $[\alpha]_D = -39^\circ.6$.

A4. A3 treated as last. $[\alpha]_D = -37^\circ.8$.

II. Preparation B; from Lappa minor.—B1. Prepared from burdock by second Tanret method. $[\alpha]_D = -40^\circ.5$.

B2. B1 dissolved in water, precipitated by alcohol to 60 per cent, boiled in 60 per cent alcohol, washed in absolute alcohol and ether. $[\alpha]_D = -38^\circ.8$.

III. Preparation C; from Dahlia variabilis.—C1. Prepared from dahlias by Dragendorff's method. $[\alpha]_D = -33^\circ.4$.

C2. C1 dissolved and precipitated by the addition of alcohol to 60 per cent. $[\alpha]_D = -36^\circ.4$.

C3. C2 dissolved and precipitated by alcohol to 60 per cent, dissolved and precipitated as before, boiled in 60 per cent alcohol, and washed with absolute alcohol and ether. $[\alpha]_D = -37^\circ.8$.

C4. C3 dissolved, precipitated with alcohol to 60 per cent, boiled in 60 per cent alcohol. $[\alpha]_D = -40^\circ.1$.

C5. C4 treated as last. $[\alpha]_D = -36^\circ.2$.

IV.—In this experiment, instead of subjecting the inulin to be polarized to the long dryings necessary to get it to constant weight, the main part of the preparation was examined air-dry and a small sample removed and a moisture determination made on it. The results were then calculated for moisture-free substance. Two preparations, one from dahlias and one from burdocks, were run along side by side. The purifications, which were the same at every step and upon both samples, consisted of solution in water, precipitation by alcohol added to 60 per cent, boiling in 60 per cent alcohol, washing in hot 60 per cent alcohol, cold 95 per cent and absolute alcohol, and finally with ether. The ether was entirely removed by drying below 100°.

D1. From burdock, Dragendorff's method. $[\alpha]_D = -37^\circ.2$.

E1. From dahlia, Dragendorff's method. $[\alpha]_D = -36^\circ.6$.

D2. From D1 as described above. $[\alpha]_D = -38^\circ.8$.

E2. From E1 as described above. $[\alpha]_D = -37^\circ.1$.

D3. From D2 as described above. $[\alpha]_D = -34^\circ.7$.

E3. From E2 as described above. $[\alpha]_D = -34^\circ.9$.

Preparations D3 and E3 were kept for three months tightly stoppered in a desiccator over sulphuric acid before they were examined in the polariscope.

Judging by the results of these experiments it seems evident that inulin preparations cannot be obtained with a specific rotation much greater than —40°. Inulin in this condition appears to be unstable, at least its rotatory power decreases on solution and reprecipitation.

Conclusions.

It appears from the investigations of others and from the experimental evidence given above that we are justified in drawing the following conclusions:

1. Inulin obtained from the underground storage organs of *Dahlia variabilis*, *Helianthus tuberosus*, *Lappa minor*, *Inula Helenium*, and *Solidago* shows no essential differences and may be looked upon as the same.

2. Inulin is accompanied in these places by levulins, resembling inulin in composition, but differing from it in possessing a greater degree of solubility and a lower specific rotation.

3. The line of division between inulin and the levulins is apparently a very difficult one to draw; the physiological significance of such a division is somewhat problematical.

4. The first method devised by Tanret is an extremely tedious process and of somewhat doubtful value for general use. The second method, although rather long, is readily enough applied, but apparently involves some loss of material and does not yield preparations having the properties of inulin as given by the author of the process.

5. Tanret claims to have isolated and determined the properties of the various levulins, but the actual laboratory experience with his methods and the products obtained thereby force one to be somewhat skeptical about the results given in Tanret's papers.

6. The results obtained in the attempts to get pure inulin, using its specific rotation as a criterion of purity, are very puzzling; they may, however, be of value in helping us to form an idea of the nature of inulin. In this connection the results of attempts to determine the molecular weight of inulin are of interest. Tanret gives to inulin a molecular weight of 4827; Brown and Morris[1] found in two trials 2159 and 2209; Ekstrand and Mauzelius[2] were unable to obtain constant results on an inulin having a specific rotation of $[\alpha]_D = -35^\circ.39$, but obtained lowerings of the freezing-point corresponding to molecular weights of from 796 to 4028. In the only determination which I have made, the depression of the freezing-point indicated a molecular weight of 2329, but when more inulin was added to the solution and the freezing-point again determined it was found to be the same as before, a very confusing and contradictory result; the inulin used had a specific rotation of $[\alpha]_D = -38^\circ.6$.

There must be some explanation for the anomalous behavior of inulin as shown by the various data given above. Perhaps we do not know enough about it to form an intelligent hypothesis, but the following conception may be helpful: The living cells of the storage organs, in polymerizing the levulose brought to them, build it up into compounds of the percentage formula $C_6H_{10}O_5$, or perhaps $6(C_6H_{10}O_5)H_2O$, perhaps both. The compounds actually formed are made up of a variable number of these radicals in loose combination. In these substances, either when within the cells or when outside of them, the great looseness of the combinations of radicals allows ready changes of size and arrangement in the molecular aggregates, rearrangements which condition small differences of properties. Thus it is conceivable that the levulins of greater solubility are made up of a smaller number of molecular nuclei in the aggregates; and that inulin, with the largest molecules, highest rotatory power, and least solubility, stands at the head of the series. Inulin itself is apparently not a single, well-defined compound, but is the name of a variety and mixture of molecular complexes, which, on account of the narrow range of differences, have been regarded as a single substance. There is a suggestion in the experimental evidence that the solubility and specific rotation of inulin do not always vary together.

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[1] "Molecular weights of the carbohydrates," J. Chem. Soc. (London), 40, 462 (1889).

[2] "Moleculargrösse einiger dem Inulin verwandter Kohlenhydrate," Chem. Ztg., 13, 1302, 1337 (1889).

May we not, in a purely empirical way, call the carbohydrate, or carbohydrate mixture, which is readily precipitated in cold alcohol of 60 per cent strength, and has a specific rotation of $[\alpha]_D = -33^\circ$ to -40° inulin; and the undetermined mixture of lower rotatory power and greater solubility, the levulin mixture?

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A RAPID METHOD FOR THE DETERMINATION OF TOTAL SULPHUR IN IRON BY EVOLUTION.

BY S. S. KNIGHT.

The recent modification of the method for determining sulphur in iron, presented by Walters & Miller, of Pittsburg, Penna., had as its principal disadvantages the extraordinarily long time, which they claim would be at least an hour, under the most favorable circumstances, to complete a sulphur determination and also the expensive and unusual apparatus for roasting samples in a current of reducing gases.

In commercial laboratories which are not equipped with this apparatus the recent modification of this roasting process has consisted in roasting the weighed sample for a period of one hour at a slowly increasing temperature. The culmination of this annealing process was the highest heat obtainable before a blast-lamp, which was continued for at least fifteen minutes. The sample thus roasted was treated as heretofore by the evolution process.

In the laboratory of the Birmingham Pipe and Casting Company, the writer has been able to get results which check very closely with those obtained by the above-described method, and also with those obtained by the barium chloride gravimetric method, by the following process:

The weighed sample, which in our case consisted of 2 grams, was mixed with 1 gram of the purest obtainable iron dust by hydrogen, and in which the sulphur content had been previously determined. This mixed sample is then placed in a small porcelain crucible and 1 gram more of the iron by hydrogen is sprinkled over the top so as to form a continuous covering. On top of this is placed a small disk of quantitative filter-paper, the lid is then placed on the crucible and this is placed on the triangle over the blast-lamp. For ten minutes the highest heat obtainable with the blast-lamp is used in roasting this mixture, at the expiration of which time it is allowed to partially cool, and the contents of the crucible are then placed in the ordinary evolution-flask and treated with hydrochloric acid, while the evolved gases are washed in any of the common forms of absorption bulbs. The absorbent liquid in our case has been an ammoniacal solution of cadmium chloride which was afterwards titrated with the iodine solution of known strength. The results obtained by this method are exactly those given by standard gravimetric methods and also the same as those obtained by Walters & Miller's method, while the time consumed is something less than one-half hour from the time the sample arrives in the laboratory.

It is believed by the writer that the advantage of this modification will be readily appreciated by chemists in charge of commercial laboratories.

BIRMINGHAM, ALA., Feb. 16, 1904.

REPORT.

Observations upon the Boiling-points of some Organic Liquids: A Method of Determining the Molecular Weights of Pure Liquids and Solids.

In an article under the above title, published in the "Annales Scientifiques de l'Université de Jassy" (March, 1901), G. G. Longinescu has pointed out that a simple relation exists between the boiling-points of organic liquids, their densities, and the number of atoms in their molecules. Reviewing the work of Kopp, he shows that the boiling-points are dependent upon the number of atoms in the molecule and the number of molecules in unit volume. Schroeder has further shown that the boiling-point depends upon the arrangement of the molecules among themselves, and upon the grouping of the atoms in the molecule. A study of the relation between the molecular weights, densities, and boiling-points of various organic liquids has led the author to the conclusion that the ratio between their boiling-points is equal to the ratio between their densities, when this latter is multiplied by the square-root of the ratio between the number of atoms in the molecules of the two substances. This relation is expressed in the equation $\frac{T}{T'} = \frac{D}{D'}\sqrt{\frac{n}{n'}}$, where T and T′ are the absolute boiling temperatures of the two liquids. D and D′ their densities at 0°, and n and n' the number of atoms in their molecules.

From this equation it follows that if the number of atoms in the molecules of two substances is the same, the boiling-points are directly proportional to their densities, a fact which he shows to hold for a long list of isomeric substances. This proportionality may also be deduced from Van der Waals' equation for "change of state."

On applying this fundamental equation to a large number of compounds, Longinescu found it to hold very closely, while where the relation did not seem to exist, previous work had shown the molecules to be associated to a considerable extent. This led him to apply the equation to the determination of the degree of association of liquids and solids.[1] By a simple transformation Equation I. becomes

$$\frac{T}{D\sqrt{n}} = \frac{T'}{D'\sqrt{n'}} = \text{constant or } n = \left(\frac{T}{C \times D}\right)^2.$$

Taking some liquids that had been shown by other methods not to be associated he calculated this constant in a number of cases, and found it to be 100.

For associated liquids a different value was obtained, the maximum value (215) being found for water. The boiling-point and density of a liquid being known, all the data are then at hand for calculating the number of atoms in the molecule.

To test the equation $n = \left(\frac{T}{C \times D}\right)^2$, it was applied to over

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[1] J. Chim. Phys., Oct., 1903.

125 non-associated liquids and gave in no case a difference of more than 2 atoms between the number as calculated and as given in the simplest chemical formula. It was further applied to liquids whose association had been determined by Ramsay, Vernon, and others, and gave results agreeing with theirs in a striking manner. Thus, the association of methyl alcohol was found to be 3.1, ethyl alcohol 2.2, propyl alcohol 1.7, acetone 1.6, while Ramsay, by his method, found for the corresponding substances 3.4, 2.7, 2.2, and 1.5.

By this method the association of formic acid was found to be 1.8, acetonitrile 3.1, aldehyde 2, nitroethane 1.4, ethylamine 1.6, glycol, 1.7, etc.

For organic solids[1] a similar relation was found to hold, D in this case representing the density and T the absolute melting-point. The value of the constant for solids was found to be 50. A large number of solids were studied, and in general the degree of polymerization in the solid state was found to be double what it was in the liquid. This would not follow, however, from the value of the constants in the two cases, because one depends upon the boiling-points and the other the melting-points.

Küster's work on the determination of the molecular weights of solids in isomorphous mixtures, is the most important work with which comparisons can be made in this field, and it is interesting to note that his results agree with those of Longinescu. For the most part the results of Longinescu with solids will have to be accepted on their face-value until confirmation is obtained.

In the application of the equation to inorganic liquids and solids[2] a difficulty was encountered in the large atomic weights of some of the elements. The weight of the molecules has an effect which the author is unable to explain, but he hopes to be able to clear up this point in a future paper. At present he limits his compounds to those made up of elements having atomic weights less than 40. For these the constants were found to be the same as for organic liquids and solids.

The agreement between his results and those of other workers is very close. Thus, liquid hydrofluoric acid was found by both Vernon and Longinescu to be four times polymerized, while they both found that there are 12 atoms in the molecule of liquid sulphur. The oxides of chlorine and nitrogen were found to be normal by Vernon, Ramsay, and Longinescu. For water the equation gave 5, while Vernon found 4.5 and Ramsay and Shields 3.5. A striking exception is noted with liquid hydrocyanic acid, which Longinescu found to be six times polymerized, while from previous work it was only supposed to be four. The new number explains much better some of the properties of the compound than the old.

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[1] J. Chim. Phys., Oct., 1903.

[2] *Ibid.*, Nov., 1903.

For inorganic solids[1] the results differ greatly, and we have no method of comparison. Most of the solids are found to be highly polymerized. Thus, hydrofluoric acid in the solid state is seven times polymerized, water 9.6, hydrocyanic acid 17.3, ammonia 10, potassium nitrate 6.8, sodium nitrate 5.2, potassium carbonate 20.1, sodium carbonate 19 8, and so on for a long list of substances.

L. S. TAYLOR.

REVIEWS.

A HISTORY OF HINDU CHEMISTRY, from the Earliest Times to the Middle of the Sixteenth Century, A. D., with Sanskrit Texts, Variants, Translation, and Illustrations. By PRAPHULLA CHANDRA RAY, D.SC., Professor of Chemistry, Presidency College, Calcutta. Vol. I. London: Williams & Norgate.

To quote from the author's preface: "The progress of chemical knowledge among the ancient nations has always had a fascination for me. * * * It was at this stage that I was brought into communication with M. Berthelot some five years ago, a circumstance which has proved to be a turning-point, if I may say so, in my career as a student of the history of chemistry. * * * But I soon found that the task was one of great magnitude. * * * In the present volume only one or two representative works of the Tantric and Iatro-chemical periods have been noticed at length."

This important work is written by an author well fitted for his task and it is hoped that the promised succeeding volumes will soon appear. Certain conclusions of value to the chemical historian should be noticed. Since Berthelot showed that true alchemy began in Egypt about the beginning of our era, the only doubt which overshadowed that conclusion was whether the origin of the Egyptian art might not at some time be found in India. This doubt seems now dispelled. The author finds no definite mention of mercury or bronzing methods before the eighth or possibly even the eleventh century. In fact, early Indian alchemy, developed in the eleventh century (by Chakrapani, 1060, and in the Rasanava) had to do not with metals, but with medicine, and is thus to be sharply distinguished from true Egyptian alchemy, though it may have been derived from it. The Iatro- or medical chemistry developed in India was transmitted directly by the Arabians into Western Europe. The author's illustrations are largely drawn from Rasaratna-samuchchaya ("alchemistic collection") of the fourteenth century, the contemporaries of which were such alchemists as Roger Bacon, "Albertus Magnus" "Raymundus Lullus," and Arnaldus, and it appears quite evident that medical alchemy was much more highly developed at that time in India, which was its source, than in Europe.

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[1] J. Chim. Phys., Nov., 1903.

The famous poison passage of Pliny is quoted as though it originated in India in the Charaka, fifth century B. C., although the only intelligible interpretation of this passage[1] seems to be an alchemistic one and there was no alchemy in India at that time.

To the historian the so-called European alchemy (from the fourteenth to the sixteenth centuries) will now appear pictured as the fusion of two streams. Egyptian alchemy, which taught the identification of the metals by their colors and the transmutation of the metals by their bronzes, was as an art destroyed by Roman edict in the third century. Out of this disaster some of the manuscripts of alchemy were saved by the Syrians and Arabians. But it was not until the medicine which they had just received from India became their principal interest that the Arabians transmitted into Europe both medicine from India and alchemistic writings from Egypt. Here medicine, transplanted from its source, failed to reach the standard attained in India; and alchemy, utterly misunderstood, was translated into medical terms. The philosopher's stone became the elixir of life. So, though the spirit of alchemy had died in Egypt, the hollow terms were used and devoutly believed and alchemy became a drag upon medicine. It was not until the sixteenth century that Iatro-chemistry in Europe was able to make its first advance, when Paracelsus, discarding the empty shell of "alchemy," routed the charlatan and proclaimed that the "object of chemistry is not to make gold but to prepare medicines."

But one question remains to be asked. Why in India did the early promise of progress in the fourteenth century come to naught? Perhaps Professor Ray will tell us this in the succeeding volumes. A. J. H.

DIE ELEKTROMETALLURGIE DER ALKALIMETALLE. Von H. BECKER, Herausgeber von "L'Industrie Elektrochimique," Paris. Monographien über angewandte Elektrochemie, IX Band. Halle, a. S.: Verlag von Wilhelm Knapp. 1903. pp. 135. Price, 6 marks.

As the title implies, there is discussed here the various methods for obtaining the alkali metals. A brief account of the chemical methods is followed by an elaborate discussion of the electrochemical. The monograph concludes with a short chapter on electrothermal procedure in obtaining the alkalies and alkaline carbides. H. C. J.

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[1] Chem. News, 1902, p. 49.

WILHELM OSTWALD. By PAUL WALDEN. Mit zwei Heliogravüren und einer Bibliographie. Leipzig: Verlag von Wilhelm Engelmann. pp. 120. 1904.

This life of Ostwald will be read with interest by all who have had the good fortune to know him, and will be especially welcomed by those who have been privileged to work with him. The life of this remarkable man is largely a history of the development of modern physical chemistry. As is well known, he was the organizer of the "Leipzig School" of Physical Chemists, the founder of their official organ—*The Zeitschrift für physikalische Chemie*—and the investigator who furnished the experimental proof of several of the generalizations upon which the "new chemistry" rests.

The author discusses the life of Ostwald in five periods. The first period (1853 to 1871) includes the boyhood and early school days of Ostwald. The second (1872 to 1875) deals with Ostwald, the student at Dorpat. The third (1875 to 1881) with him as teacher in Dorpat. The fourth (1881 to 1887) period tells us of Ostwald the professor in Riga, and the fifth is the Leipzig period.

As Walden points out, much work was done during the Riga period, but the greatest activity was shown after settling down in Leipzig. Here Ostwald was in the very center of scientific activity, and his genius received unlimited stimulus from his surroundings. Further, he saw a new day for chemical science, to be inaugurated largely through his own efforts. Van 't Hoff had pointed out the fundamental relations between solutions and gases, and Arrhenius had proposed the Theory of Electrolytic Dissociation. Ostwald saw the consequences of these generalizations, probably, as no one else had done, and began to apply them in all directions in physics and chemistry. Under his guidance Nernst made use of them in solving the problem of the primary cell.

A large number of students began to migrate to Leipzig, and with their aid Ostwald worked out experimentally the suggestions that had come to him.

Most of the striking characteristics of Ostwald have been faithfully portrayed by Walden. Perhaps one or two additional points may be referred to. Ostwald always impressed the writer of this review as having a control of physical and chemical literature that was simply wonderful—matters which other men of far maturer years knew where to find, Ostwald had always at his finger's end. This seemed to apply to almost every phase of Physics, Inorganic Chemistry, and Physical Chemistry.

A personal characteristic which made a lasting impression on us all was the absolute lack of selfishness in our teacher. Investigation after investigation was suggested to us, and when complete we were told to publish it as if it were of our own thinking. This characteristic was so pronounced as to call for special comment.

May the life of Ostwald just written by Walden be but the preface to the longer life of scientific activity which yet remains to him. H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE CHEMIE, VII. CYANID-PROZESSE ZUR GOLDGEWINNUNG. Nach einschlägigen Quellen bearbeitet von MANUEL VON USLAR, dipl. Hütteningenieur, unter Mitwirkung von DR. GEORGE ERLWEIN, Vorstand der elektrochemischen Abteilung der Siemens und Halske A. G., Berlin. Mit 30 Figuren und 13 Tabellen im Text und 3 Tafeln. Halle a. S.: Verlag von Wilhelm Knapp. 1903.

In this book of 100 pages and four chapters, besides the introduction, is given much of interest concerning the cyanide process of obtaining gold. The first chapter gives an account of the McArthur Forest and the Siemens-Halske processes. The next describes the methods in actual use in seven works, including the dimensions of the tanks, the amount of cyanide used, the charge per tank, etc. The relative cost is also stated. The fourth chapter, about one-half of the book, is devoted to the modifications of the process. Of most interest to the chemist who is not a specialist in this line is the third chapter, which discusses the chemistry of the process. When gold dissolves in a solution of potassium cyanide two reactions take place:

$$(1)\quad 2Au + 4KCN + 2H_2O + O_2 = 2KAu(CN)_2 + 2KOH + H_2O_2;$$

$$(2)\quad 2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$

The metal must be in a finely divided state, and even then it will not dissolve if the oxygen of the air is excluded. Upon the latter fact are based a number of patents that are chiefly of scientific interest and of little practical importance. The influence of other constituents of the ore are taken up also. The elements, antimony, arsenic, and tellurium are up to the present "Schmerzenskinder" for those engaged in the cyanide process, for no cheap and practicable way of dealing with them has been devised. Zinc blende and lead compounds exert an unfavorable influence, as do also iron sulphate and other salts formed by weathering. Carbon dioxide from the air sets hydrocyanic acid free, and even the oxygen may do harm, although it is necessary, as shown above. An excess of it acts in this way:

$$(1)\ KCN + O = KCNO;$$
$$(2)\ 2KCNO + 3O = K_2CO_3 + CO_2 + N_2;$$
$$(3)\ 2KCN + CO_2 + H_2O = K_2CO_3 + 2HCN.$$

When the gold is in solution it is precipitated by adding metallic zinc. According to the equation,

$$2KAu(CN)_2 + Zn = 2Au + Zn(CN)_2(KCN)_2,$$

1 gram of zinc should precipitate about 6 grams of gold, but here again, on account of side reactions, 40 grams are needed to throw down 6 grams of gold. The chapter includes an account of the analytical methods used at the different works.

C. E. W.

DIRECTIONS FOR LABORATORY WORK IN PHYSIOLOGICAL CHEMISTRY. By HOLMES C. JACKSON, PH.D., Assistant Professor of Physiological Chemistry in the University and Bellevue Hospital Medical College. Second edition. New York: John Wiley & Sons. 1903. pp. 148.

The author has added much new material in this edition. The experiments, which are clearly described, are not fully explained so that the student has to make out the meaning of the experiments for himself. The book is not unique in any particular but conforms to the usual type of manuals on laboratory practice in physiological chemistry.

A. S. L.

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CHEMICAL JOURNAL

A NEW ELECTRIC FURNACE AND VARIOUS OTHER ELECTRIC HEATING APPLIANCES FOR LABORATORY USE.[1]

BY H. N. MORSE AND J. C. W. FRAZER.

Having found in the electrolytic process[2] a ready and satisfactory means of depositing semi-permeable membranes, and having overcome, to some extent, the mechanical difficulties which are encountered in assembling, in a secure manner, the various parts of the osmotic cell, we turned our attention to the third, and probably the most difficult, problem which must be solved before any attempt to devise a practicable method for the direct measurement of osmotic pressure can succeed—namely, to the porous wall on which the semi-permeable membrane is deposited.

Thin sections of the walls of the cells in which the high pressures recorded elsewhere[3] had been developed, as well as of cells which had conducted themselves unsatisfactorily, were studied under the microscope, and it was found that there are certain well-marked characteristic differences of porous wall structure between those cells which conduct themselves well and those in which it is impossible to develop any considerable pressure.

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[1] The work of the authors, undertaken with the purpose of perfecting, if possible, a practicable method for the measurement of osmotic pressure, has been carried on with the aid of grants from the Carnegie Institution. The present article describes some of the incidental results of that work.

[2] This JOURNAL, **26**, 80; **28**, 1; **29**, 173.

[3] *Ibid.*, **28**, 1.

These differences will be described more fully in a later article in connection with an account of our attempts to produce in the laboratory a porous clay wall suitable for the construction of osmotic cells. It is sufficient, for present purposes, to state that we soon found, in the course of our study of thin sections, that probably one reason for the more or less complete failure of more than nine-tenths of the porous vessels made at the potteries is the too rapid expulsion of the chemically combined water during the baking of the clay, which results in the production, by the escaping steam, of relatively large channels through the wall material. The openings of these channels on the interior surface of the vessels are spanned—not filled—by the membrane, and when the membrane is subjected to pressure it is ruptured at the unsupported points.

It appeared that some method of baking must be devised which would make practicable a very precise regulation through the range of temperatures within which clay loses the greater portion of its water. The electric furnace in which the resistance of platinum wire is utilized to secure high temperatures appeared likely to answer our purpose, and we procured one of a type which has had some currency in this country. In it the wires are threaded through holes in the interior of the sides and bottom of the furnace so that the heat generated in the wires must penetrate a considerable thickness of clay before reaching the space to be heated. With such an arrangement it requires a very long time to obtain, with any given current, the temperature which that current will eventually maintain in the furnace. In the case of the instrument here mentioned, from seven to nine hours were required to reach a constant temperature with a constant current, and close regulation was therefore impossible. Another objection to this furnace was its wastefulness. At 1250° the consumption of electrical energy was equivalent to 1200 watts. A little above this temperature the sheet-iron casing burned out and was replaced by one of baked fire-clay, provision being made for an air space between it and the furnace proper. The furnace behaved somewhat better thereafter, both in respect to the time required to reach a constant temperature and the amount of current necessary to maintain it. But the improvement was not sufficient to justify its employment for our purposes and it was discarded.

The defects of the abandoned furnace were due to the faulty principles on which it was constructed—to the burial of the wires within the walls of the space to be heated, and to the absence of vacant enclosed spaces between it and the outer air. In the furnace about to be described these faults are avoided. The furnace represented by the accompanying figures is not that which is employed by us as a kiln for the burning of clay vessels, but is one which was designed for the fusion of materials, *e. g.*, silicates, in crucibles. It, however, does not differ from the kiln except in respect to dimensions and the fact that in the kiln—owing to its larger size—two wires in parallel are employed, while in the smaller instrument a single wire suffices, or, if two are present, they are generally used in series.

The furnace proper is represented by Fig. I. The three hard-burned perforated clay rings, *a*, *b*, and *c*, are held in place by three platinum rods made from No. 16 wire (B & S gauge). The ends of these rods are threaded, and each end is provided with two small platinum nuts, between which the rings *a* and *c* are firmly fastened. The purpose of the ring *b* is to keep the crucible from coming in contact with the platinum wires. It is adjustable up or down, but may be fixed in any desired position by twisting short pieces of wire about the rods. The internal diameters of *b* and *c* are equal, while that of *a* is smaller in order to furnish a rest for the crucible support. Each ring is provided with 60 perforations, in two rows of 30 each, through which the wire (No. 26 B & S gauge) is woven up and down in the manner shown in the figure. The inner row of wires also crosses from side to side under *a*. The

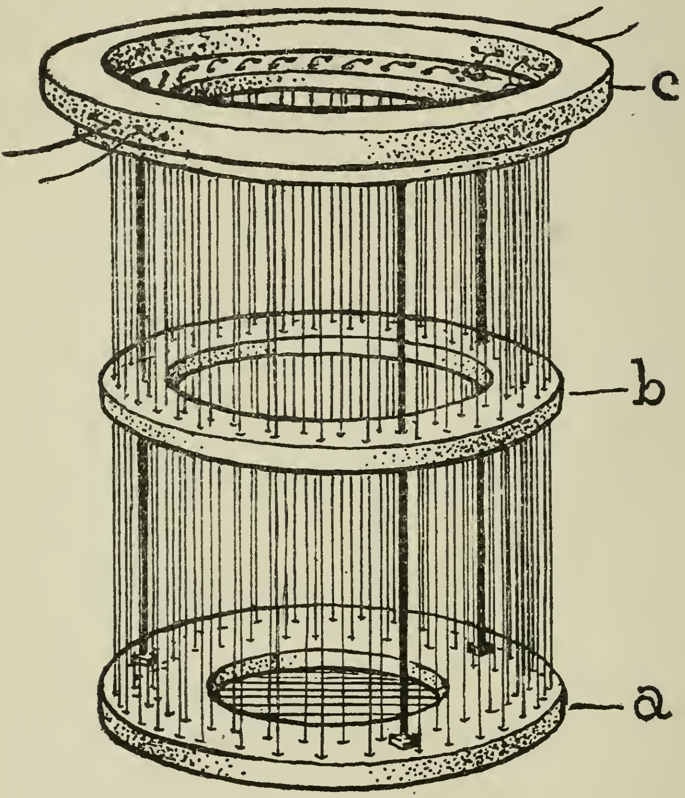

Fig. I.

total height of the furnace as represented in Fig. I. is 80 mm. and the total length of the wire is 16 feet. The platinum rods serve two important purposes. They support the whole weight of the furnace and its contents and thus prevent any stretching of the wires while hot, and, having at all times about the same temperature as the wires, they keep them perfectly straight and thus prevent any danger of short circuits through contact of adjacent strands.

The furnace as represented in Fig. I. is surrounded by the clay cylinder *d*, as shown in Fig. II., the ring *c*, Fig. I., resting upon the upper edge of *d*. The cylinder *d* is provided with the perforated cover *e* and the bottom *f*, which rests upon the three truncated clay cones, *g*. The perforation in *e* serves for the introduction of a thermometer or pyrometer.

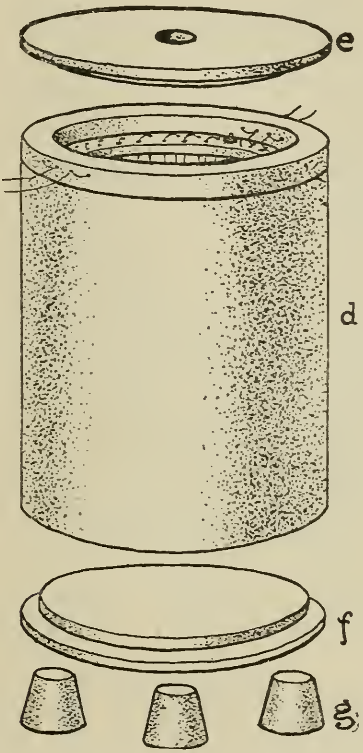

Fig. II.

Fig. III. represents a cylinder, *h*, of larger dimensions, which surrounds *d*. It is also furnished with a perforated cover, *i*, a bottom, *j*, and the supports *k*.

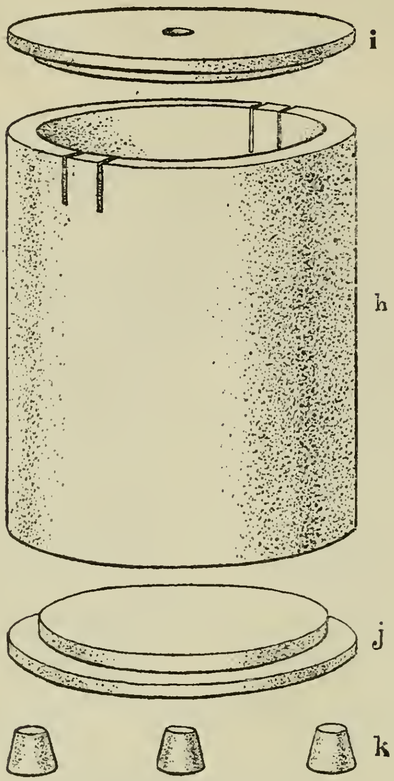

Fig. III.

The complete furnace is shown in Fig. IV., in which *l* is a Le Chatelier pyrometer, *m* a galvanized iron cylinder with cover—both of which are lined and covered with asbestos paper, *n* a series of asbestos boards with ventilating spaces between them, *o* a block of soapstone, and *p* a board on which the whole arrangement rests and can be moved without disturbing any of the parts. *q* and *r* are firmly fixed steel rods which serve to connect the wires coming from the furnace with the external circuit and to protect the former from in-

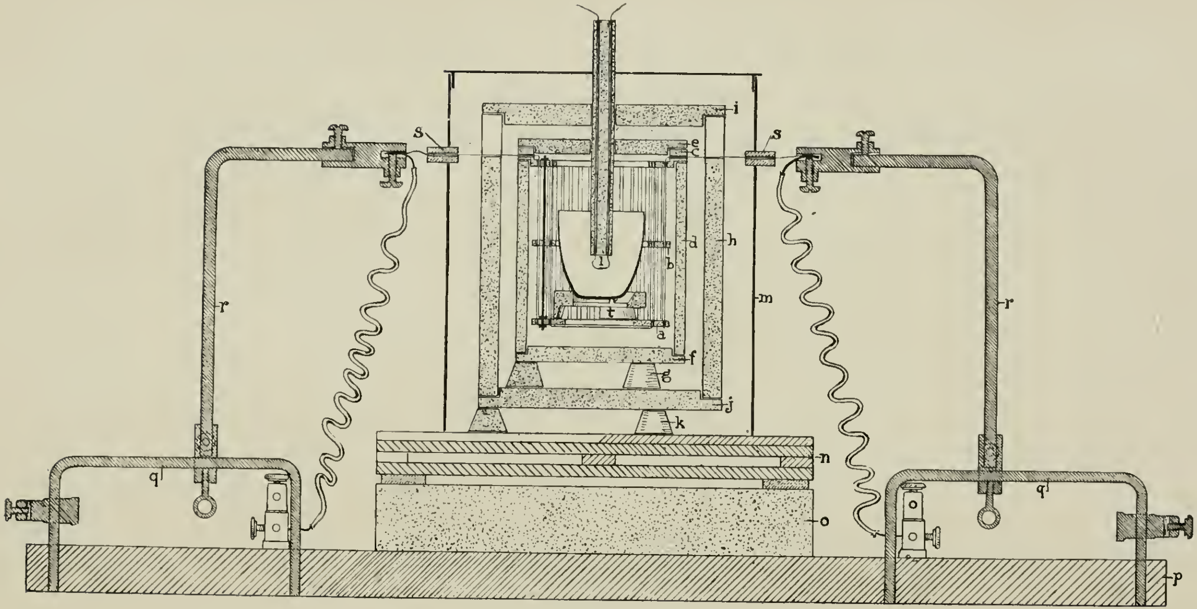

Fig. IV.

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jury through strains of any kind. *s,s* are short pieces of pipe stem which keep the platinum wires from contact with the metallic cylinder *m*. The crucible support *t* is made as light and open as possible, coming in contact with the crucible at three points only.

The material which was used in making the clay parts of the furnace was a mixture of equal portions by weight of a fire-clay from Mt. Savage, Md., and a clay from Edgar, Fla. Neither of these materials, taken alone, was suitable for the purpose. The fire-clay was lacking in adhesive qualities and crumbled easily after baking, unless heated to a very high temperature, while articles made of the clay from Florida exhibited a tendency to crack, both during the air-drying and the baking periods. The mixture of the two was easily formed and the moulded pieces were quite free from a tendency to crack, either while drying in the air or during the burning process. The burned products were very tough and remained porous at high temperatures, and therefore showed little tendency to stick to the platinum wires. The clay from Florida had already been washed in the manner usual in preparing such material for the potteries. The coarser matter in the fire-clay was removed by sifting, and the two clays were thoroughly mixed by passing them repeatedly through a fine sieve. The smaller articles—the rings and the inner cylinders with their covers—were burned in the laboratory in a Seger experimental furnace, while the larger outer cylinders were burned for us at the pottery of D. F. Haynes & Son, to whom we are indebted for many other courtesies during the course of our work.

Since any one who wishes to reproduce this furnace or to provide himself with a similar one will probably have to act as his own potter, it may be of service to enter somewhat into mechanical details. The making of the perforated rings, *a*, *b*, and *c*, is the most troublesome part of the task though it presents no very great difficulties.

In the hard wood block *a*, Fig. V., a cavity is turned on the lathe which has the form and dimensions of the ring *c* when first molded—allowance having been made, of course, for the shrinkage of the clay in burning. The holes for the two rows of wires and the three posts are then bored and into each hole is inserted a closely fitting steel rod *b*—pieces of small knitting needles being used for the purpose. The cavity is filled with plaster of Paris, giving the piece *c* upon which in turn, with the rods in place, the plaster cast *a*, Fig. VI., is made. The pieces *b* and *c*, Fig. VI., are of hard wood and are turned to correct form and dimensions on the lathe. The parts *a* and *b* are fastened together by the bolts *d*,*d*. When the ring *e* is to be made, the clay is moulded into its place in *a*, *b* is bolted to *a*, and *c* is crowded into position. The perforations in the ring are then made by pushing the needles through the holes in *a*. Finally, the excess of the clay,

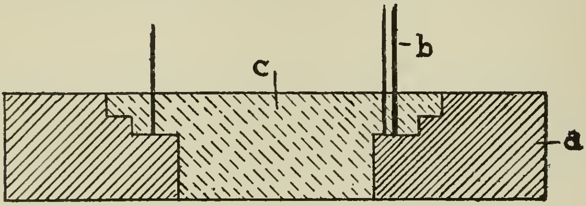

Fig. V.

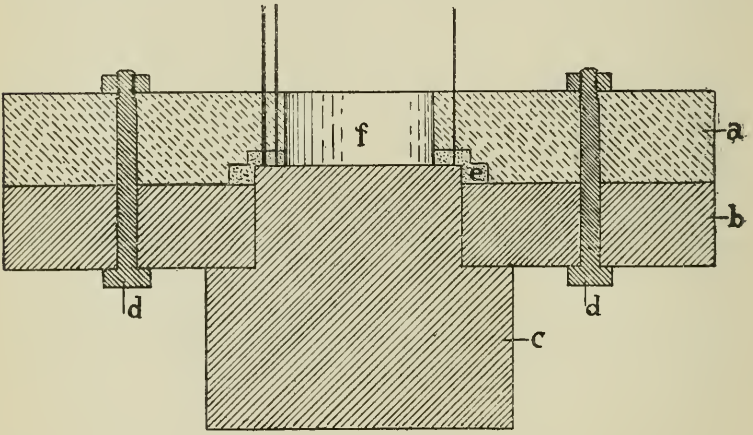

Fig. VI.

which, by the procedure described, has all been crowded into the cavity *f*, is trimmed away, leaving the inside of the ring round and smooth. The description here given relates to the upper ring *c*, Fig. I. The middle and bottom rings are made in a similar manner and the process need not, therefore, be explained.

Fig. VII. represents the form of mold in which the cylinders *d* and *h*, Figs. II. and III., are made. *a* is a circular hard wood core whose external diameter is equal to the internal diameter of the clay cylinder, except at the ends, where it is equal to the external diameter of the cylinder. *b* is a ring which may be removed. The core *a* is tapered slightly toward the end having the ring in order to facilitate its withdrawal after molding the clay. *c* and *c* are the two halves of a plaster of Paris mold which are held together by the bolts *d*,*d*. The wet clay is rolled out flat and to the right thickness, cut to shape, and wrapped about the wooden core which has previously

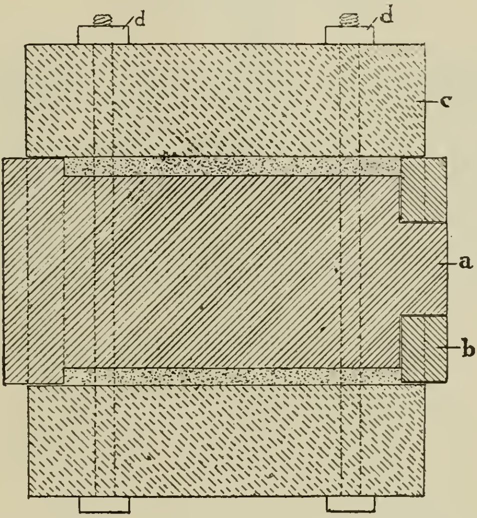

Fig. VII.

been covered with oil to prevent sticking. In order to perfect the outside of the cylinder, the core with the clay on it is rolled along the table top and then placed in the plaster mold. As soon as the clay becomes sufficiently stiff, the core is withdrawn.

Fig. VIII. represents the arrangement for making the tops and the bottoms of the cylinders. *a* is a hard wood block, *b* is a block of plaster of Paris which has been cast about a model of a top or bottom, and *c* is a cork borer which is used to cut a hole when a top is to be made.

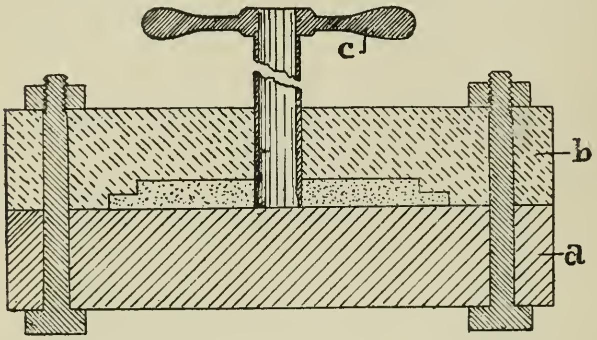

Fig. VIII.

The wiring of the furnace is accomplished in the following manner: The wire is straightened out and fastened at the two ends. A current is then sent through it until it glows throughout its entire length. Or, with the wire in one hand and a lamp in the other, it is heated to redness, section by section, from end to end. Either process will remove a tendency on the part of the wire to wind up or twist, but the first is the better method because a wire which has been treated in the second way will exhibit irregular resistance, owing to unequal stretching of the different parts while hot. After threading the wire through the three holes belonging to each vertical strand, the strand is heated to redness with the flame of the lamp or, better, by means of an electric current, and while the wire is hot and under a slight strain it is fastened in place by inserting a steel pin in the last hole, which must not be removed until after the succeeding strand has been finished in the same manner. If a little pains is taken in these matters, every strand will be perfectly straight and the furnace, when finished, will present a neat and satisfactory appearance.

The first step to be taken with the completed furnace is to calibrate it, that is, to determine its resistance for every temperature up to the limit to which it is afterwards to be heated, for it will then be feasible at all times, without the aid of a pyrometer, to maintain in it with certainty any desired temperature or to ascertain at any time what the temperature in it is. The furnace, in fact, becomes by virtue of such a calibration a resistance pyrometer.

For the calibration of the kilns used in the baking of cells and of the laboratory furnace just described we had at our disposal mercury thermometers registering to 550°, a Le Chatelier platinum platinum-rhodium pyrometer, and a Keiser-Schmidt decimillivoltmeter, all of which had been tested at the German Physikalisch-Technische Reichsanstalt. We give below in tabular form the data for the crucible furnace up to 967°. The calibration was not carried higher because the temperature 950° is sufficient for any ordinary crucible work. The temperatures given are probably correct to within 5° or less. The voltmeter which was used to measure the electromotive force developed at the junction of the platinum and platinum-rhodium wires is furnished with two scales, one in which each division has the value of a decimillivolt, and another in which a division corresponds to 20° of temperature. Unfortunately the needle of this instrument is unnecessarily thick and clumsy near the free end, making possible some errors of parallax in reading. These, however, could not amount to more than one-fourth of a division on either scale. The ammeters and voltmeters used in measuring the current were of the best Weston types.

Current.	Voltage.	Resistance.	Watts.	Temperature.
2.5	33.7	13.48	84.25	383°
2.6	36.0	13.846	93.60	407°
2.7	38.5	14.259	106.38	434°
2.8	41.0	14.671	114.80	463°
2.9	43.6	15.034	126.44	488°
3.0	47.4	15.80	142.20	526°
3.1	50.2	16.193	155.62	558°
3.2	52.7	16.468	168.72	587°
3.3	55.3	16.757	182.49	615°
3.4	58.3	17.147	198.22	640°
3.5	61.2	17.486	214.20	663°
3.6	64.3	17.861	231.48	690°
3.7	66.9	18.081	247.53	710°
3.8	70.1	18.447	266.38	741°
3.9	73.3	18.795	285.87	766°
4.0	76.3	19.075	305.20	793°
4.1	79.5	19.390	325.55	813°
4.2	82.5	19.643	338.25	840°
4.3	85.3	19.837	366.79	867°
4.4	88.7	20.159	390.28	888°
4.5	92.0	20.444	414.00	914°
4.6	95.0	20.652	437.00	940°
4.7	98.0	20.851	460.60	967°

It will be readily understood that an accurately calibrated resistance furnace is theoretically an admirable instrument for the study of reactions at high temperatures, for, if external conditions are constant, it will always require the same amount of electrical energy to maintain any given temperature in the empty furnace, or, what is the same thing, a given amount of electrical energy is bound to maintain in it always a certain fixed temperature. If now any reaction involving the disappearance or evolution of heat takes place within the heated space, the amount of electrical energy required to maintain the temperature at which it takes place will be increased or diminished, according as the reaction is endothermic or exothermic, and the difference, if it can be ascertained, will serve as a measure of the heat energy of the reaction.

There is little difficulty in discovering at what temperatures reactions involving any considerable heat effects take place in an electric furnace. In baking our cells, for example, while the water is being expelled from the clay the amount of current required to maintain a given temperature is very noticeably larger than that required to maintain the same temperature in the empty kiln, showing that a reaction involving the loss of heat is going on within. Again, when a fusible substance is heated in the furnace and the temperature of fusion is reached, there is noticed an increase in the flow of the current without any corresponding increase in the resistance of the platinum wire, *i. e.*, in the temperature of the furnace. The increased flow of current continues for a time and then diminishes to its original volume, showing that the fusion is finished. If the furnace has been calibrated, a determination of its resistance during the time of the increased flow of current will give the melting-point of the substance. In this way we found the fusing-point of sodium carbonate to be between 860° and 863°. The exact time of fusion may also be ascertained by arranging to have the sinking of a platinum weight into the softened material either close or break a circuit in which there is a sensitive ammeter.

In order that the results of the study of reactions by means of the electric furnace may have a high degree of precision, certain difficulties must be overcome. The principal one of these is the length of time required to establish equilibrium between the temperature within the furnace and that of the external air. During the calibration of the furnace under consideration, we raised the current each time by 0.1 ampere, which gave an average rise of temperature of about 26°.4 for each increase of current, the minimum being 20° and the maximum 38°. Usually about one-half of the rise occurred within the first five minutes, while the remainder occupied from fifty to sixty minutes with a gradually decreasing rate, which finally became very slow.

The tardiness of this adjustment between internal and external temperature conditions—despite the favorable location of the wires with respect to the space heated and the double enclosed air spaces surrounding it—lessens the precision of the results when the furnace is employed to determine fusing-points and to ascertain the temperatures at which reactions (loss of water, etc.) occur, and a remedy is called for. The most promising remedy which suggested itself was to cover the exterior of the furnace, where it is in contact with the outer air, with some substance which conducts electricity, but whose conductivity increases with rise in temperature, and to divide the circuit so that while the major portion of the current passes through the furnace, another portion passes over and heats the surface in contact with the air. The effect of such an arrangement would be to compensate automatically for the increased loss of heat to the outer air which attends any rise in the temperature of the furnace, for as the temperature rises, the conductivity of the circuit through the furnace would diminish, while that of the outer circuit would increase and a larger proportion of the total current would therefore take the latter course.

Since graphite is a substance which not only conducts electricity, but one whose conductivity increases with rise in temperature, it seemed likely to be of service in our scheme, and we began to test the suitability for heating purposes of surfaces covered with that material. One result of this work has been the construction of a number of air-baths for general use in the laboratory, some of which we will here describe.

Soapstone is undoubtedly the best of all available materials on which to spread the graphite for heating purposes. It is easily cut to any desired form, its surface can be made very smooth, which is essential to the best results, and, above all, it withstands better than any other non-conducting material great and sudden changes of temperature.

We take pleasure in acknowledging here our indebtedness to the Alberene Stone Company, which provided us, free of expense to ourselves, with an abundance of this material, and also to the Joseph Dixon Crucible Company, which presented us with liberal quantities of different varieties of specially prepared graphite.

Figs. IX. and X. represent two forms of graphite stoves for ordinary hot-air baths. *a*, Fig. IX., is a soapstone block of convenient size for the usual rectangular copper hot-air bath.

It is seen in place in Fig. XI. *b,b,b,b* are strips of iron which are bolted to the block at the ends, the central bolt at each end serving for the attachment of the wires of the circuit.

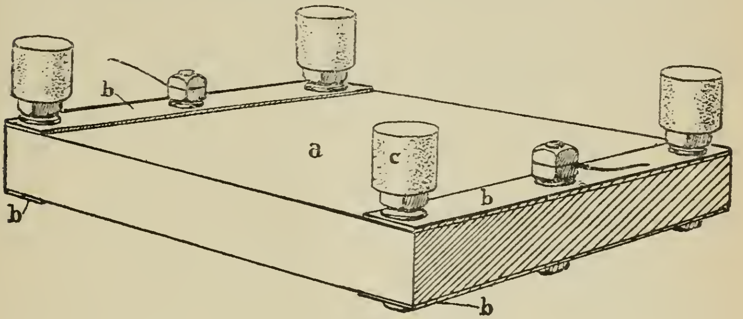

Fig. IX.

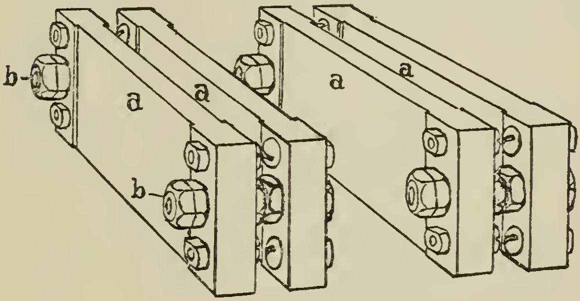

Fig. X.

The corner bolts, which are longer than the others, are covered by the soapstone pieces *c,c,c,c*. On these rests the perforated metallic shelf, as seen in Fig. XI.

Fig. X. represents another arrangement for heating the same bath, which has the advantage that the surfaces on which the heat is generated are vertical. *a,a,a,a* are narrow strips of soapstone of such dimensions that when bolted together by twos, as shown in the figure, three pairs of them can rest on the bottom of the bath, leaving room between the ends for the insertion of mica plates to prevent electrical contact. Each end of every soapstone strip is provided with two iron plates which are bolted to the stone in the manner shown. Two strips, thus furnished, are fastened together by the longer bolts *b*,*b*, which are also utilized for the attachment of wires.

Fig. XI. represents the arrangement as a whole. *b* is a copper-bath of the usual form, having a mica window in its door. The stove *a*, which may be of either of the forms represented in Figs. IX. and X., rests on the soapstone strips *c*,*c*. The inner vertical walls of the copper bath may be lined to advantage with thin asbestos board, but in that case it is

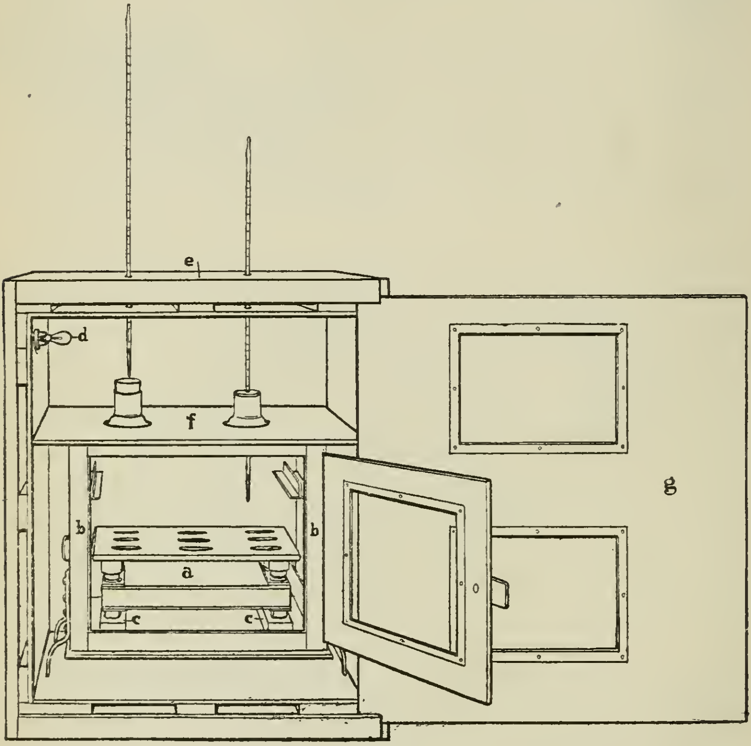

Fig. XI.

well to cover the exposed surface of the board with aluminium paint, which will prevent the lodgment of dust and the shedding of particles of asbestos. The wires of the stove pass horizontally through the sides of the copper bath and the outer compartment to the exterior of the wooden box which encloses the whole, where each wire terminates in a binding post screwed into the box. Where the wires pass through the copper walls they are prevented from coming in contact with the metal by short pieces of clay pipe stem. When a stove such as is shown in Fig. X. is used, each of the three pairs of plates is provided with independent wires and binding posts, any required combinations of the individual pairs in parallel or series being made more conveniently on the outside than on the inside of the bath. *d* is a diminutive electric lamp of small voltage, which serves to illuminate the scales of the thermometers. The current for it comes through a shunt from the stove, and a switch is fastened to the outside of the box for the purpose of closing and breaking the lamp circuit. The voltage of the lamp must be suited, of course, to the fall in potential of the stove. The interior of the wooden box is lined on all sides, except the front, with asbestos board in such a manner as to leave confined air spaces between the asbestos and the wood. The surface of the lining boards is also covered with aluminium paint. *f* is a closely fitting shelf of asbestos board (also painted), which rests upon the copper bath and is supported at the ends. *g* is a door which slides in grooves in the wooden box. It contains two mica windows and is made from asbestos board.

The shelf *f* divides the interior of the box into two compartments whose temperatures will differ quite widely from each other and from the temperature which is maintained within the copper bath. This difference can, however, be diminished, if desired, by replacing *f* by a more or less open shelf which permits circulation of air between the upper and lower spaces. Each of the heated compartments, including the copper bath, should be provided with two properly located ventilating tubes running to the outside of the wooden box. Porcelain insulating tubes are well adapted for this purpose. They may be closed with corks, to prevent loss of heat, when not needed.

Fig. XII. is a cross-section of a furnace used by the authors

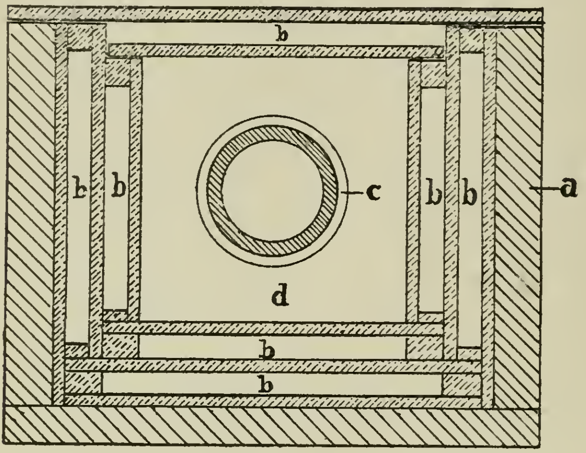

Fig. XII.

for heating substances enclosed in tubes (Carius tubes, etc.). *a* is a wooden box 625 mm. in length, which is so lined and covered with asbestos board as to give the closed air spaces designated by *b*. *c* is a porcelain tube having the length of the box and an internal diameter of 30 mm. The space *d* about *c* is sufficient to accommodate larger tubes when required to do so. An iron tube of thin wall is slipped into *c* to aid in distributing the heat and to prevent injury to the porcelain tube when explosions occur. Fig. XIII. shows an iron collar which is fastened to each end of the porcelain tube and serves for the attachment of the wires.

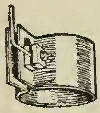

Fig. XIII.

The rubbing of ground, dry graphite upon the smooth surface of soapstone or porcelain does not give a sufficiently heavy coating of the material to conduct the requisite amount of current. A thicker covering of graphite can be obtained by repeated applications of it, in a wet condition, with a flat camel's hair brush. The surface to which it is applied must, however, be hot enough to evaporate the water almost instantaneously, otherwise the deposit will be quite uneven. The results obtained by the last method are nevertheless unsatisfactory. The material lacks adhesiveness and when an attempt is made to harden it by polishing with a stiff brush, much of the graphite is detached and the surface which is produced is easily injured by handling or by contact with other objects.

Better results are secured by mixing the ground graphite with washed and bolted clay and making a paste of the mixture with water. But the best results have been obtained with the paste form of a well-known stove polish,[1] and we shall describe somewhat in detail our method of applying it since a correct procedure in this matter is of much importance. The iron plates at the ends of the soapstone block (Fig. IX.) or of the strips (Fig. X.) are removed, and their inner surfaces, and also those portions of soapstone which are covered by the plates, are evenly spread with a rather thick layer of the paste. The plates are then replaced and bolted together. The block or strip (connected in the circuit in which there is also an ammeter) is placed on a piece of asbestos board or of some other non-conducting material, which is heated by a lamp. When the stone is hot enough to evaporate water with rapidity, but without "sputtering," the paste, much thinned with water, is evenly applied with a flat camel's hair brush whose width is about 25 mm. The whole stone should be covered each time, but the brush should not pass more than once over any one spot. After each application, the surface is vigorously polished with a stiff tooth-brush.

An even distribution of the graphite is of great importance, for, if it is unevenly distributed, the resistance in different regions will vary and more heat will be developed at some points than others. The result, in the case of a carelessly prepared stove, is that the graphite burns out in certain spots while the whole amount of heat developed is much less than the surface ought to bear with safety.

As soon as the conductivity of the graphite covering has increased to a point where the current suffices to maintain the proper temperature of the stove, it is removed from the asbestos board and the surface is carefully explored with the voltmeter with reference to the uniformity of the distribution of resistance. The subsequent applications of the graphite are regulated with a view to securing uniform conductivity over the whole surface, that is, those spots which are found by the voltmeter to exhibit a higher resistance are painted more thickly than the others. With care and a little experience, it becomes easy to prepare in a short time a stove on which the graphite is very evenly distributed and so firmly adherent that it will not visibly soil the fingers in handling. As the painting proceeds, the surface is apt to become so hot that the water is evaporated with explosive violence, and the surface presents a spotted appearance, owing to an uneven spreading of the material. When this occurs, the circuit must be broken and the stone allowed to cool before making an application.

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[1] The "Rising Sun."

The thickness of the graphite covering should be regulated with a view to the most economical expenditure of energy in the subsequent use of the stove, in other words, with a view to dispensing with as much as possible of the external resistance which is always inserted in the circuit for the purpose of regulating the temperature of the bath. In this connection, the advantage of the stove represented in Fig. X. will be seen. It consists, as has already been stated, of three sections of two plates each, each section having its two wires running to the outside of the wooden box, where they terminate in binding posts. With such an arrangement, it is easy, as a rule, to make a combination of the sections which will suit the voltage of the current which is to be used and therefore to reduce to a minimum the amount of external resistance required for the regulation of the bath. In preparing the stove of this kind which we have in use, the application of the graphite to each strip was continued until, with a fall of potential of 50 volts, it conducted one ampere of current. The temperature of the stone at the time of finishing the strips was not always the same, so that the resistance at any given temperature varies somewhat from strip to strip, but not sufficiently to lead to difficulties.

It is important for users of graphite baths to know approximately what temperature a graphite surface will bear without injury. It is unfortunate that an admixture of clay is necessary in order to improve its spreading and adhesive qualities, for the clay begins to lose its water at about 425°, and at this point a change in the resistance of the material occurs. Speaking generally, it may be stated that the temperature of the stove itself should not be allowed to rise above 400°. How nearly the temperature of a bath may be made to approach this limit will depend, of course, upon the volume of the space to be heated as compared with the area of the heating surface. In small baths we have succeeded in keeping a constant temperature of 400°, but there is danger that, in attempting to reach so high a temperature too quickly, the clay will become overheated and lose some of its water. We have found it safe and practicable with properly prepared stoves having a suitable area of heating surface to maintain in a considerable variety of baths any temperature up to 350°. A somewhat higher temperature may be maintained, but always at some risk to the stove. The principal danger lies in using too large a current while raising the temperature of the bath.

We give below the data relating to some of the baths which we have in use in order that a judgment may be formed respecting the economical advantage of using electricity rather than gas for ordinary laboratory purposes.

Bath No. 1 was like that shown in Fig. XI. The stove was of the kind represented in Fig. IX. The temperature to which the bath was tested was 250°, which is as high as a copper bath should be heated. The temperatures given in the first column are those of the copper bath, while those in the second column are the temperatures of the upper compartment. The third column gives the current; the fourth, its fall of potential within the bath; the fifth, the number of watts consumed; and the sixth, the number of hours which a kilowatt will maintain the temperatures recorded in the first and second columns.

Bath No. 1.

Temperature in copper bath.	Tempera- in upper compartment.	Current. Amperes.	Fall in potential. Volts.	Watts.	Hours per kilowatt.
100°	48°	1.73	15.9	27.5	36.36
125°	58°	2.10	18.8	39.48	25.58
150°	65°	2.50	21.4	53.50	18.69
175°	72°	2.77	23.2	64.26	15.56
200°	85°	3.16	25.5	80.58	12.41
225°	96°	3.48	27.0	93.96	10.75
250°	106°	4.07	29.2	118.84	8.41

Bath No. 2 differed from No. 1 only in that a stove of the kind represented in Fig. X. was used. It was tested between 150° and 258°.

Bath No. 2.

Temperature in copper bath.	Temperature in upper compartment.	Current. Amperes.	Fall in potential. Volts.	Watts.	Hours per kilowatt.
150°	73°.0	1.20	40.3	48.36	20.67
175°	83°.5	1.39	44.5	61.85	16.10
200°	95°.0	1.61	49.0	78.89	12.60
225°	104°.5	1.89	51.5	97.33	10.20
258°	111°.0	2.53	50.0	126.50	7.90

The cost of keeping the baths Nos. 1 and 2 at the temperatures given in the tables is very small. It will depend, of course, upon the price paid for the electricity, but even at the extreme current prices per kilowatt, the heating of such baths by electricity is more economical than heating them by gas. In addition to the cost of the source of the heat, we have to consider, in a problem of this kind, the relative destructive effects of the two methods upon the copper-baths; and, here again, there is a considerable advantage in favor of the use of electricity rather than gas. The electricity used in this institution is produced at an expense of 2.5 cents per kilowatt. This estimate covers interest on cost of plant, an allowance of 10 per cent for deterioration of machinery and building, average expense of current repairs, labor, and fuel. At 2.5

cents per kilowatt, the cost of maintaining bath No. 1 for a day of eight hours is: at 100°, 0.55 cent; at 125°, 0.78 cent; at 150°, 1.07 cents; at 175°, 1.29 cents; at 200°, 1.61 cents; at 225°, 1.86 cents; and at 250°, 2.38 cents. There must be added, of course, the losses due to the external resistance which is inserted in the circuit for purposes of control, but these need not be large if the conductivity of the stoves is regulated with reference to the voltage of the currents which must be used.

Where electricity is employed as the source of heat, baths made of soapstone would be more serviceable than are the copper ones in ordinary use. The former would be more cleanly and durable than the latter and could be heated to higher temperatures. According to some preliminary estimates in the hands of the authors, the first cost of baths of soapstone would be only slightly greater than of baths of copper.

A new graphite stove, when first used in its bath, should be made to maintain for several hours a somewhat higher temperature than the highest for which it was designed before any calibration of the bath is undertaken. The resistance at any given lower temperature is thereafter fairly constant. In any subsequent use of the bath, the current should never be allowed to exceed that which was employed in the preliminary heating.

Graphite, in quantities sufficient for heating by the current, may be made to adhere to a smooth surface like that of porcelain or soapstone by mixing with it a small amount of soap, and the temperature which such a covering will sustain without any marked alteration of conductivity is quite surprising. A quantity of finely pulverized electrotyping graphite was made into a thick paste by mixing it with a small amount of a concentrated solution of soap, and with this mixture, a porcelain tube, for use in the bath represented in Fig. XII., was prepared. The data obtained in testing the tube are given in the table which follows:

Porcelain Tube.

Temperature.	Current. Amperes.	Fall of potential. Volts.	Watts.	Hours per kilowatt.
150°	1.54	28.5	43.89	22.8
175°	1.74	31.7	55.66	17.9
200°	1.96	35.6	69.77	14.3
225°	2.07	37.4	77.42	12.9
250°	2.34	42 0	98.28	10.2
275°	2.59	45.0	116.55	8.6
300°	2.79	49.2	137.27	7.3
355°	3.38	55.3	186.91	5.3

Conducting surfaces made from the mixture of graphite with soap are not as satisfactory as those made from the stove polish we have used. They are more easily injured by scratching, and it is more difficult to secure a uniform distribution of the former than of the latter material.

For baths in which higher temperatures are to be kept than can safely be produced by a graphite stove, we employ the arrangement shown in Fig. XIV., in which the resistance of small platinum wire is utilized to generate the heat. *a* is a soapstone block of any size to suit the dimensions of the bath, with bolts near two opposite sides, which serve to fix the coils in their places and for the attachment of the wires of the circuit. Four of the bolt ends are covered with the soapstone caps *b*. The purpose of the caps will be made apparent by an inspection of Fig. XI. The length and size of the platinum wire are made to suit the conditions which are to be met—the size of the bath, the temperature to which it is to be heated, the voltage of the available source of current, etc. In the fur-

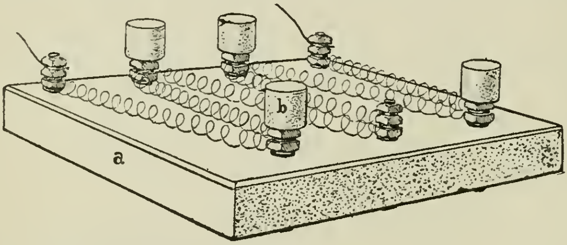

Fig. XIV.

nace shown in the figure, the wire is No. 32 (B & S gauge) and 8 feet long. To prepare the wire, it is straightened, heated to redness by the current, and then wound on a threaded steel rod of the proper diameter. Such furnaces may, of course, be used in the place of the graphite stoves previously described, and the following table gives the data which were obtained while testing one of them in a bath arranged as shown in Fig. XI., except that the shelf *f* in this case was perforated so as to permit free circulation of air between the upper and lower compartments:

Bath with Platinum-wire Stove.

Temperature in copper bath.	Temperature in upper compartment.	Current. Amperes.	Fall of potential in bath. Volts.	Watts.	Hours per kilowatt.
100°		1.08	28.5	30.8	30.5
125°	72°	1.24	34.9	43.3	23.1
150°	80°	1.4	41.8	58.5	17.1
175°	89°	1.6	51.0	81.6	12.3
200°	110°	1.77	59.8	105.9	9.5
225°	125°	1.89	66.4	125.5	8.0
250°	144°	2.0	73.0	146.0	6.9

Fig. XV. shows a bath with platinum stove which was constructed for the purpose of heating rather large vessels to any temperature up to 500°. The heating coils of the stove *a* contain about 16 feet of No. 26 platinum wire; *b* is a terra cotta cylinder like those used in chimneys for stove pipes; *c* is a sheet-iron cylinder, which is covered inside and outside with asbestos paper; *d* and *d* are covers of asbestos board; *e* is a terra cotta receptacle such as is used for flower pots; *f* is sand in which the stove and the lower ends of *b* and *c* are embedded. The dimensions of the free heated space within the bath are 250 and 175 mm. For the sake of cleanliness and of improved appearance, *e*, *c*, *d*, and the outside of *b* are covered with aluminium paint. With temperatures within up to 300° it is safe to surround the outer cylinder *c* with woolen material, or better, with a thick pad made of hair. When higher temperatures are to be maintained, we employ, in place of the pad, a wooden cylinder with an internal diameter equal to the extreme width of the base *e*, and cover it with a strip of

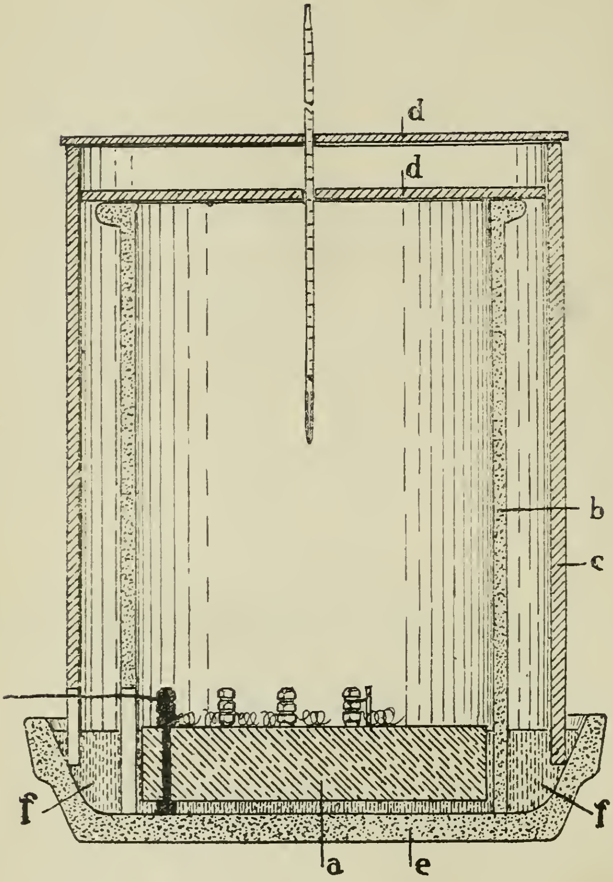

Fig. XV.

woolen cloth. A test of this bath to 400°, with the thermometer bulb located in the center of the heated space, gave the following data :

Temperature.	Current. Amperes.	Fall of potential. Volts.	Watts.	Hours per kilowatt.
100°	2.08	20.7	43.06	23.22
125°	2.20	23.0	50.60	19.76
150°	2.45	28.0	68.60	14.58
175°	2.70	32.3	87.21	11.47
200°	2.85	35.7	100.75	9.92
225°	3.04	40.8	124.03	8.06
250°	3.09	43.0	132.87	7.53
275°	3.29	48.5	159.57	6.27
300°	3.50	53.5	177.25	5.64
350°	3.73	61.0	227.53	4.40
400°	4.0	68.0	272.00	3.67

We have not tested the bath beyond 400° except to determine that, with a current pressure of 110 volts, its temperature rises above 500°.

Arrangements like that just described are an effective substitute for all of the oil and paraffin baths which give so much offense in the laboratory, and, like all electrically heated baths, they have the great advantage that, with a current of constant voltage, they can be regulated with a high degree of precision.

The foregoing are only types of the numerous electrically heated baths which we have devised for use in the laboratory, but they will suffice to illustrate both the practicability and the economy of substituting electricity for gas in many laboratory operations.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON PHENYLMALONIC NITRILE.

[PRELIMINARY PAPER.]

BY JOHN C. HESSLER.

A previous paper, entitled "On Alkyl Malonic Nitriles and Their Derivatives,"[1] described the preparation and properties of ethylmalonic and benzylmalonic nitriles and their sodium and silver salts. A study of the decomposition of these salts made it appear very probable that the metal is bound to nitrogen. It was hoped that further evidence regarding the linking of the metal in substances of this class might be obtained from the salts of phenylmalonic nitrile, consequently the preparation of this substance was attempted.

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[1] This JOURNAL, **22**, 169.

Phenylmalonic nitrile was made from phenylcyanacetamide, which, in turn, was prepared from phenylcyanacetic ether.

Preparation of Phenylcyanacetic Ether.

The method used for preparing phenylcyanacetic ether was a condensation of benzyl cyanide with carbonic acid ethyl ester by means of sodium.

The carbonic ether was made from Kahlbaum's chlorcarbonic ether and alcoholic sodium ethylate. It boiled at 125° C. The benzyl cyanide used was Kahlbaum's preparation. It boiled at 226° C.

Ten and nine-tenths grams of sodium, in wire form, were put into a solution of 56 grams of carbonic ether (one gram-molecule) in 350 cc. of absolute ether. There was only a very slight action. Then 56 grams (the theoretical amount) of benzyl cyanide were added in several portions. Hydrogen began to escape at once, and the sodium was colored golden-yellow. The temperature soon rose to the boiling-point of the ether; consequently the flask was kept cool (by means of running water) until the greater part of the sodium had gone into solution. The mixture was then allowed to stand for about twelve hours. The reaction-product separated out as a yellow solid. The supernatant ether was brown.

Dilute sulphuric acid was now added, and the yellow solid went into solution. The ethereal layer was separated, washed with water, and dried over calcium chloride. After the distillation of the ether a brown oil remained. This was distilled at reduced pressure (25 mm.) with the following result:

Fraction.	Temperature.	Weight. Grams.
1	Up to 115° C.	3.0
2	115° to 150°	10.1
3	150° to 170°	15.6
4	170°	22.5
5	170° to 180°	19.8

Three grams of tar remained in the distilling-flask.

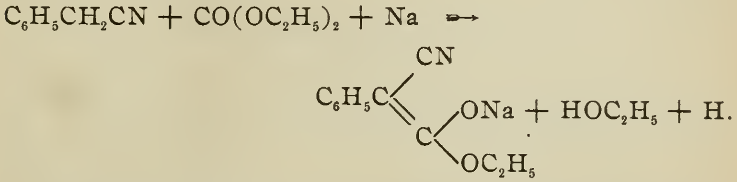
A redistillation of fractions 2 to 5, inclusive, gave 50 grams of a practically colorless oil boiling at 160° to 170° (chiefly at 164° to 165°) at 17.5 mm. A portion was specially purified for analysis, and proved to be phenylcyanacetic ether.

I. 0.1778 gram substance gave 0.4561 gram CO_2 and 0.0969 gram H_2O.

II. 0.2494 gram substance gave 16.7 cc. N_2 at 18°.5 C. and 741.1 mm.

	Calculated for $C_{11}H_{11}O_2N$.	Found. I.	Found. II.
C	69.84	69.96	....
H	5.82	6.06	....
N	7.41	....	7.55

The formation of phenylcyanacetic ether is probably represented by the equation



$$C_6H_5CH_2CN + CO(OC_2H_5)_2 + Na \rightarrow C_6H_5C(CN){=}C(ONa)(OC_2H_5) + HOC_2H_5 + H.$$

The lower-boiling fractions (1 and 2) consisted chiefly of carbonic ether and benzyl cyanide. That the reaction is not complete is probably due to the fact that some of the sodium reacts with the alcohol formed in the condensation.

Properties.—Phenylcyanacetic ether is a colorless oil insoluble in water, but readily miscible with organic solvents. It boils at 165°.5 C. at 20 mm. At the ordinary pressure it boils at 275° C. with only slight decomposition. The specific gravity of the substance is 1.09 at 22° C. (Westphal).

Phenylcyanacetic ether is not affected by cold, dilute acids, but it dissolves readily in aqueous alkalies. If the alkaline solution is acidified at once the ester may be recovered, but after standing some hours it is saponified to phenylcyanacetic acid (*q. v.*). The ester dissolves readily in ammonia solution, giving, after some time, crystals of phenylcyanacetamide.

Sodium Salt of Phenylcyanacetic Ether.—An absolute ethereal solution of phenylcyanacetic ether reacted vigorously with sodium, forming the sodium salt. This separated as a white powder. After twenty-four hours it was filtered off, washed with absolute ether, dried for five minutes on a clay plate, and then *in vacuo* over sulphuric acid and caustic potash.

I. 0.2708 gram substance gave 0.0861 gram Na_2SO_4.
II. 0.3246 gram substance gave 0.106 gram Na_2SO_4.

	Calculated for $C_{11}H_{10}O_2NNa$.	Found. I.	II.
Na	10.9	10.3	10.58

The sodium salt of phenylcyanacetic ether is a hygroscopic substance. Its dilute alcoholic solution gives a white precipitate with silver nitrate solution, but the precipitate soon turns black.

Preparation of Phenylcyanacetamide.

Phenylcyanacetic ether (42.2 grams) was treated with 49 grams of concentrated ammonia water. The ester went entirely into solution, and the mixture became warm and somewhat colored. After several hours the mixture was practically solid. The crystals of the amide were then filtered off, washed with water, and dried on a clay plate. The weight obtained was 24.5 grams, instead of 35.7 grams, the theoretical amount.

Properties.—Recrystallized from absolute alcohol, the amide melts at 147° C. It is practically insoluble in cold water, very difficultly soluble in ether, and only slightly soluble in cold alcohol. In hot absolute alcohol it dissolves readily, separating from the cooled solution in large crystals.

Phenylcyanacetamide dissolves readily in cold 10 per cent caustic soda solution, giving off ammonia. The sample used for analysis was recrystallized from absolute alcohol and dried *in vacuo* over sulphuric acid.

0.155 gram substance gave 0.3841 gram CO_2 and 0.0719 gram H_2O.

	Calculated for $C_9H_8ON_2$.	Found.
C	67.5	67.58
H	5.0	5.15

Preparation of Phenylmalonic Nitrile.

Eight grams of phenylcyanacetamide and 4.2 grams of phosphorus pentachloride were mixed in an Anschütz flask. The flask was exhausted to 23 mm. and then heated to 120° to 125° C. in a metal-bath. A reaction began almost at once and continued for about ten minutes. When the mixture was in quiet fusion, the temperature of the bath was raised until the phenylmalonic nitrile distilled over. It collected in the side tube of the flask as a liquid, but soon solidified. The weight of the crude product was 4.2 grams, *i. e.*, about 60 per cent of the theoretical amount. Much tar remained in the distilling-flask. The proportions of phenylcyanacetamide and phosphorus pentachloride used correspond to 5 molecules of the amide and 2 of the pentachloride.[1]

A portion of the phenylmalonic nitrile was crystallized from dilute alcohol and dried *in vacuo* over sulphuric acid. It melted at 68° to 69° C.

I. 0.1524 gram substance gave 0.4224 gram CO_2 and 0.0652 gram H_2O.

II. 0.1273 gram substance gave 22.6 cc. N_2 at 23° C. and 751.2 mm.

	Calculated for $C_9H_6N_2$.	Found. I.	II.
C	76.06	75.59	....
H	4.22	4.75	....
N	19.72	....	19.88

Properties.—Phenylmalonic nitrile is difficultly soluble in water and in ligroin, but readily soluble in alcohol and in ether. It crystallizes from dilute alcohol in large, white crystals. It crystallizes well, also, from a mixture of ether and ligroin (40° to 60°). From the fused condition phenylmalonic nitrile crystallizes in hexagonal plates. The substance boils undecomposed at 152° to 153° C. at 21 mm.

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[1] This JOURNAL, **22**, 181; Hesse: *Ibid.*, **18**, 726.

Action of Alkalies on Phenylmalonic Nitrile.

Phenylmalonic nitrile is not readily saponified, even by concentrated alkalies, and differs greatly in this respect from benzylmalonic nitrile.[1]

Eight-tenths gram of the substance was dissolved in a large excess of 10 per cent caustic soda solution and left for twenty-four days. An excess of dilute sulphuric acid was then added and the resulting precipitate of phenylmalonic nitrile was filtered off, washed with water, and dried on a clay plate. The substance recovered weighed 0.45 gram. It melted at 68° C. The recovered phenylmalonic nitrile was then heated to boiling with 10 per cent caustic soda for ten minutes. Not a trace of ammonia was evolved. When the solution was acidified as before, 0.38 gram of the substance was recovered.

Finally, the substance (0.38 gram) was left standing with an excess of alcoholic caustic potash for four days, and the mixture was afterwards heated to boiling thirty minutes under a reflux condenser. Water and sulphuric acid were then added, the solution was extracted with ether, and the ether extract was washed with water and dried with calcium chloride. When the ether was distilled off, 0.3 gram of phenylmalonic nitrile was recovered.

Phenylmalonic nitrile is soluble in aqueous sodium carbonate, and is extracted by it from ether solution. Aqueous solutions of phenylmalonic nitrile give precipitates with solutions of copper sulphate, mercuric chloride, and silver nitrate.

Sodium Salt of Phenylmalonic Nitrile.—Phenylmalonic nitrile (3.8 grams) was dissolved in 75 cc. absolute ether and treated with 0.8 gram (an excess) of sodium in wire form. The reaction was rather slow, but was accelerated by the addition of 1 drop of absolute alcohol. After sixteen hours the unused sodium was picked out and the precipitated sodium salt was filtered off, washed with absolute ether, and dried *in vacuo* over sulphuric acid. The yield was 4 grams, *i. e.*, about 90 per cent of the theoretical. An analysis gave the following result:

0.3055 gram substance gave 0.1347 gram Na_2SO_4.

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[1] This JOURNAL, 22, 181.

	Calculated for $C_9H_5N_2Na$.	Found.
Na	14.02	14.28

The sodium salt of phenylmalonic nitrile is white when freshly made, but when left over sulphuric acid *in vacuo* for several days it becomes violet. It reacts very slowly, if at all, with methyl and ethyl iodides under ordinary conditions. The aqueous solution of the sodium salt gives back phenylmalonic nitrile when acidified. The aqueous solution also gives precipitates with solutions of barium chloride, lead acetate, copper sulphate, silver nitrate, and mercuric chloride.

An attempt to get the sodium salt from benzene solution did not succeed. Five grams of phenylmalonic nitrile, dissolved in 50 grams of benzene, were treated with 1.5 grams (an excess) of sodium wire, and left for four months. Practically no action took place, as was shown by the fact that 4.8 grams of phenylmalonic nitrile were recovered.

Silver Salt of Phenylmalonic Nitrile.—All attempts to prepare the silver salt of phenylmalonic nitrile have failed, owing to its instability. This fact is evident from the following experiments:

Six and six-tenths grams of phenylmalonic nitrile were dissolved in 200 cc. of 50 per cent alcohol, cooled in iced water, and treated with a solution of 7.9 grams (1 molecule) of silver nitrate in 50 per cent alcohol. The silver salt separated out as a white, bulky precipitate, but in a few minutes it became, first, steel-blue and then light-brown in color. It was filtered off, washed with water, and dried on a clay plate and *in vacuo* over sulphuric acid. The weight obtained was 11 grams, or practically the theoretical amount. When the product was treated with ether it was found that the ether extracted organic material. Accordingly, the residue was heated with ether five times under a reflux condenser. The residual powder had the appearance of reduced silver, but still contained organic material. This fact was shown by the ignition of two samples, after they had been dried *in vacuo*.

I. 0.7406 gram substance gave 0.6351 gram Ag, or 85.75 per cent.

II. 0.5825 gram substance gave 0.4991 gram Ag, or 85.68 per cent.

The residue was then extracted four times more with boiling ether and dried *in vacuo*. Ignition of a sample gave the following result:

0.4273 gram substance gave 0.3788 gram Ag, or 88.65 per cent.

During every ignition the solid first became dark, then lost a sharp smelling, red vapor, and finally became coal-black. Heating with the blast-lamp for a long time was necessary to make the silver residue white.

When the combined ether extracts were distilled, a gummy solid remained. This turned red in moist air and in aqueous solution. When dried on a clay plate it was found to be amorphous and almost white. The substance was dissolved in ether and the solution treated with ligroin (40° to 60°). A portion was thus precipitated. When it had been dried *in vacuo* it melted at 147° to 148°.

A second attempt, in which the phenylmalonic nitrile was first treated with the theoretical quantity of sodium hydroxide, gave the same general results. A solution of 1.42 grams of phenylmalonic nitrile in 50 per cent alcohol was treated with 10 cc. (the theory) of normal caustic soda solution and then with 1.7 grams of silver nitrate dissolved in dilute alcohol. The silver salt was precipitated, but changed as before.

0.3324 gram substance gave, on ignition, 0.1471 gram Ag.

	Calculated for $C_9H_5N_2Ag$.	Found.
Ag	43.37	44.25

The high percentage of silver was undoubtedly due to the fact that some of the organic material remained in solution in the dilute alcohol.

Boiling ether extracted from the product the same substance as was formed in the first experiment. When this substance was precipitated from ethereal solution by means of ligroin (40° to 60°), it melted as before, at 147° to 148°.

Two carbon and hydrogen determinations of different preparations of the substance gave practically identical results. A nitrogen determination was also made.

I. 0.0791 gram substance gave 0.2225 gram CO_2 and 0.027 gram H_2O.

II. 0.1602 gram substance gave 0.4504 gram CO_2 and 0.0541 gram H_2O.

III. 0.1241 gram substance gave 21.4 cc. N_2 at 21° C. and 755.8 mm.

	Calculated for		Found.		
	$C_9H_6N_2$.	$C_9H_5N_2$.	I.	II.	III.
C	76.06	76.59	76.71	76.68	....
H	4.22	3.55	3.79	3.75	....
N	19.72	19.86	....	....	19.61

The substance burned with difficulty, and the last portions of the nitrogen came off only at red heat. This may account for the fact that the percentage of nitrogen was low.

The nature of all the substances formed when silver nitrate reacts with phenylmalonic nitrile is being investigated. The body melting at 147° to 148° seems to be only one of several products.

Phenylcyanacetic Acid.

Preparation.—Phenylcyanacetic acid was prepared by the saponification of its ethyl ester. The ester was dissolved in ether, and the solution was shaken with sodium hydroxide. After the alkaline solution had stood over night it was acidified with dilute sulphuric acid, and the separated acid was extracted with ether. There was obtained an almost colorless oil, which solidified on cooling. After it had been dried on a clay plate the solid melted at 62° to 65°.

That the substance was phenylcyanacetic acid was shown by converting it into its silver salt. Some of the crude product was dissolved in a slight excess of ammonia, and the excess was removed *in vacuo* over sulphuric acid. A solution of silver nitrate (a slight excess) was then added. The silver salt separated as a white, curdy precipitate, which soon became granular. A silver determination, by ignition, gave the following result :

0.3191 gram substance gave 0.128 gram Ag.

	Calculated for $C_9H_6NO_2Ag$.	Found.
Ag	40.29	40.11

When the crude acid, melting at 62° to 65°, was recrystallized from ether-ligroin, the melting-point was raised about 10°. After two recrystallizations from hot benzene the substance was dried *in vacuo* over sulphuric acid. It then melted sharply at 92° C.

0.1663 gram substance gave 0.41 gram CO_2 and 0.072 gram H_2O.

	Calculated for $C_9H_7O_2N$.	Found.
C	67.08	67.24
H	4.35	4.81

Properties.—Phenylcyanacetic acid is soluble in water, alcohol, ether, and hot benzene; insoluble in ligroin. When heated in a bath at 150° to 160° it decomposes, giving carbon dioxide and benzyl cyanide.

Action of Phenylmalonic Nitrile with Methyl Ioaide and Alcoholic Sodium Ethylate.

Phenylmethylcyanacetimido Ethyl Ester.—Two grams of phenylmalonic nitrile in absolute alcoholic solution were treated with 0.32 gram (1 atom) of sodium, also dissolved in absolute alcohol. Three grams of methyl iodide (1.5 molecules) were then added. The temperature of the mixture rose to 32° C. After forty minutes the alcohol was distilled off, water was added, and the separated oil was extracted with ether. The ether solution was washed with sodium hydroxide solution and with water, and was dried with calcium chloride. Distillation of the ether left a colorless oil, which was distilled *in vacuo*. The yield was 2.4 grams, or practically theoretical.

An analysis gave the following results:

I. 0.2075 gram substance gave 0.5428 gram CO_2 and 0.1304 gram H_2O.

II. 0.1947 gram substance gave 24.5 cc. N_2 at 18° C. and 740.3 mm.

	Calculated for $C_{12}H_{14}ON_2$.	Found. I.	II.
C	71.29	71.34	....
H	6.93	6.99	....
N	13.86	....	14.21

The imido ether is a faintly aromatic oil boiling at 152° to 153° at 16 mm. and at 158° to 159° at 22 to 23 mm. Its specific gravity is very nearly 1.06 at 23° C. The substance is insoluble in water, but dissolves readily in alcohol and in ether. The alcoholic solution instantly gives a precipitate of ammonium chloride when treated with concentrated hydrochloric acid.

Action of Phenylmalonic Nitrile with Benzyl Chloride and Alcoholic Sodium Ethylate.

Phenylbenzylmalonic Nitrile.—Two grams of phenylmalonic nitrile, dissolved in absolute alcohol, were treated with 0.32 gram (1 atom) of sodium, also in alcoholic solution, and with 2.5 grams (an excess) of benzyl chloride. The temperature of the mixture rose, and sodium chloride separated out. After the mixture had been heated under a reflux condenser for thirty minutes the alcohol was distilled off and the residue was treated with water and extracted with ether. The ethereal solution was washed with caustic soda solution and dried with calcium chloride. Evaporation of the ether left phenylbenzylmalonic nitrile. The crude substance (3.5 grams) was crystallized from ether-ligroin and from absolute alcohol. It melted in each case at 97° to 98°.

0.17 gram substance gave 0.5154 gram CO_2 and 0.0841 gram H_2O.

	Calculated for $C_{16}H_{12}N_2$.	Found.
C	82.76	82.68
H	5.17	5.49

Phenylbenzylmalonic nitrile crystallizes from ether-ligroin in long needles grouped in feathery masses. It is easily soluble in ether and in alcohol, but practically insoluble in ligroin and in water. It is not affected by aqueous alkalies, even at 100° C.

Phenylbenzylcyanacetic Ethyl Ester.—Five and seven-tenths grams of phenylcyanacetic ether, in 20 cc. of absolute alcohol, were treated with 0.7 gram (1 atom) of sodium in 25 cc. of absolute alcohol. The temperature rose and the mixture became red. Then 3.8 grams (1 molecule) of benzyl chloride were added. The temperature rose still more, and sodium chloride separated out slowly. The mixture was heated under a reflux condenser for three hours, the sodium chloride filtered off, and the alcoholic solution distilled. There were obtained 7.4 grams of an oil boiling at 231° to 233° at 32 mm. and at 216° to 217° at 16 mm. An analysis resulted as follows:

I. 0.186 gram substance gave 0.5268 gram CO_2 and 0.1076 gram H_2O.

II. 0.5512 gram substance gave 24.4 cc. N_2 at 15°.5 C. and 757.5 mm.

	Calculated for $C_{18}H_{17}ON_2$.	Found. I.	Found. II.
C	77.42	77.24	....
H	6.09	6.43	....
N	5.02	....	5.17

Phenylbenzylcyanacetic ether is a thick, colorless liquid having the sp. gr. 1.13 at 22° C. In a freezing-mixture and in an outside room at winter temperature it became so viscous that it could not be poured, but it would not crystallize. The substance is insoluble in water and is not affected by aqueous alkalies.

The study of phenylmalonic nitrile and its derivatives is being continued in this laboratory.

CHICAGO, January 25, 1904.

Contributions from the Sheffield Laboratory of Yale University.

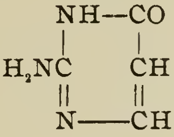
CXV.—RESEARCHES ON PYRIMIDINES. SYNTHESIS OF 2-AMINO-5-METHYL-6-OXYPYRIMIDINE.

[SIXTH PAPER.]

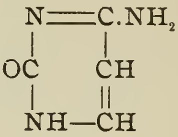
BY TREAT B. JOHNSON AND SAMUEL H. CLAPP.

In a previous paper from this laboratory, Wheeler and

Johnson[1] described the two monoaminooxypyrimidines which can give uracil on hydrolysis, *viz.*, 2-aminooxypyrimidine (Formula I.), and 2-oxy-6-aminopyrimidine or cytosine (Formula II.):

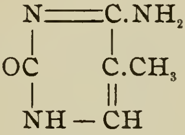


I.

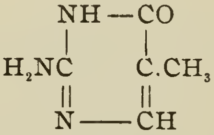


II.

In a similar manner the two monoaminomethylpyrimidines which could give thymine on hydrolysis are, *viz.*, 2-oxy-6-amino-5-methylpyrimidine (Formula III.) and 2-amino-6-oxy-5-methylpyrimidine (Formula IV.):



III.



IV.

Wheeler and Johnson[2] in a recent paper have described 2-oxy-6-amino-5-methylpyrimidine (Formula III.) and have shown that it is more or less readily converted into thymine on hydrolysis.

We will describe in this paper the second monoaminomethylpyrimidine (Formula IV.), which theoretically could give thymine on hydrolysis, *viz.*, 2-amino-5-methyl-6-oxypyrimidine. We have synthesized this aminopyrimidine by condensing guanidine with the sodium salt of formylethylpropionate. We have not only been able to obtain the pyrimidine base which we desired, but have also succeeded in isolating intermediate products in the reaction. These have given us a more thorough insight into the mechanism of these pyrimidine condensations.

We find, namely, that in this condensation there are three steps in the reaction—first a condensation of guanidine with the formyl group of the sodium formylethylpropionate giving an acrylic ester (Formula V.), then a saponification of the acrylic ester to the free acid (Formula VI.), and finally a condensation to the pyrimidine with loss of a molecule of water :

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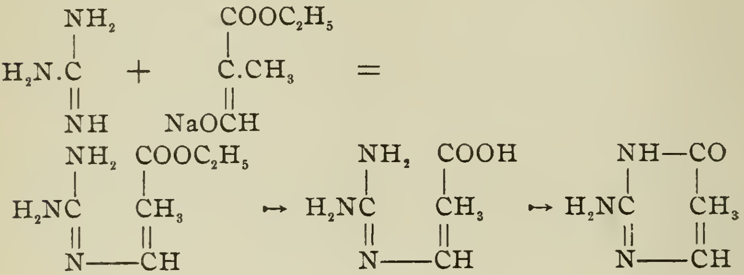
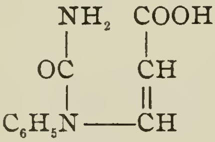
[1] This JOURNAL, **29**, 492 (1903).

[2] *Ibid.*, **31**, 592 (1904).

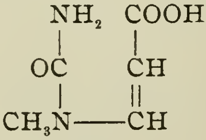


V. VI.

Under the conditions by which we worked we did not observe the formation of the intermediate guanidineacrylic ester, but have evidence of its existence because of the fact that we have been able to isolate the intermediate guanidinemethylacrylic acid. Müller[1] has described two substituted acrylic acids that are analogous to our intermediate acid. He found that phenylurea and methylurea readily condensed with oxalethylacetate, giving a phenyluracilcarboxylic ester and methyluracilcarboxylic ester. By dissolving these two esters in alkali and treating with strong hydrochloric acid they were decomposed into uramidoacrylic acids (Formulas VII. and VIII.) :



VII.



VIII.

Behrend,[2] in his synthesis of methyluracil from acetoacetic ester and urea, was able to isolate an intermediate uramidocrotonic ester, but was unable to isolate the free acid from its sodium or potassium salt on account of the ease with which it condensed to the pyrimidine.

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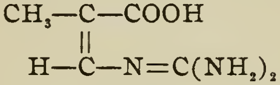
[1] J. prakt. Chem., 56, 475.

[2] Ann. Chem. (Liebig), 229, 8.

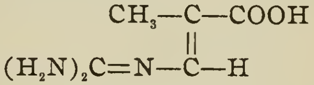
We, furthermore, have made the interesting observation that our intermediate α-methyl-β-guanidineacrylic acid is capable of existing in two isomeric modifications. One acid melts at 331° to 332° C. with violent effervescence; the other at 318° to 320° C. to a clear oil. Both acids can be converted by treatment with alkali into the 2-amido-5-methyl-6-oxypyrimidine.

It appears to us that the explanation for this interesting case of isomerism is that we are dealing with an ethylene linking, and have another case of *cis* and *trans* isomerism:



$$\begin{array}{l} CH_3-C-COOH \\ \qquad \| \\ \quad H-C-N=C(NH_2)_2 \end{array}$$

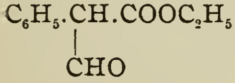
IX.
Cis.



$$\begin{array}{r} CH_3-C-COOH \\ \| \qquad \\ (H_2N)_2C=N-C-H \qquad \end{array}$$

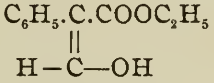
X.
Trans.

Wislicenus[1] was able to isolate three isomeric modifications of formylphenylethylacetate. He represented their structure as follows:



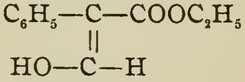
$$\begin{array}{l} C_6H_5.CH.COOC_2H_5 \\ \qquad | \\ \quad CHO \end{array}$$

XI.



$$\begin{array}{l} C_6H_5.C.COOC_2H_5 \\ \qquad \| \\ H-C-OH \end{array}$$

XII.



$$\begin{array}{l} C_6H_5-C-COOC_2H_5 \\ \qquad \quad \| \\ HO-C-H \end{array}$$

XIII.

He furthermore showed that the *enol* form was capable of forming isomeric salts, which gave isomeric acyl modifications when treated with acyl chlorides.

In a later paper Wislicenus and Bindemann[2] showed that analogous acyl modifications could be obtained from the sodium salt of formylethylacetate. Finally, Wislicenus[3] extended his investigations to the sodium salt of formylethylpropionate, which we used in our condensation, and observed that this also gave stereochemical isomers when treated with acyl chlorides. The close analogy between Wislicenus' isomers and our modifications is shown by the following formulas:

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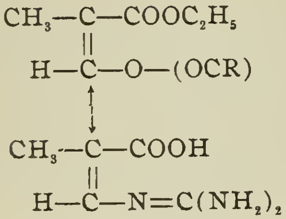
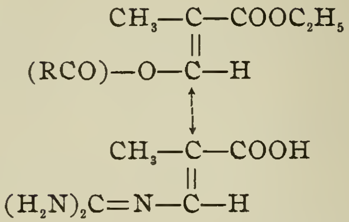
[1] Ann. Chem. (Liebig), **312**, 33.

[2] *Ibid.*, **316**, 18.

[3] *Ibid.*, **316**, 333.

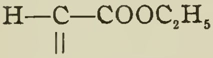


$$\begin{array}{l} CH_3-C-COOC_2H_5 \\ \qquad\;\| \\ \;\;H-C-O-(OCR) \\ \qquad\;\updownarrow \\ CH_3-C-COOH \\ \qquad\;\| \\ \;\;H-C-N=C(NH_2)_2 \end{array}$$



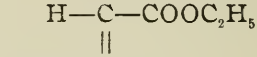
$$\begin{array}{r} CH_3-C-COOC_2H_5 \\ \| \qquad\qquad\; \\ (RCO)-O-C-H \qquad\qquad\; \\ \updownarrow \qquad\qquad\; \\ CH_3-C-COOH \qquad\;\; \\ \| \qquad\qquad\; \\ (H_2N)_2C=N-C-H \qquad\qquad\; \end{array}$$

It seems probable to the writer that Pechmann's[1] isomeric derivatives which he obtained by treating the sodium salt of formylethylacetate with aniline and paratoluidine are to be explained in a similar manner:



$$\begin{array}{l} H-C-COOC_2H_5 \\ \quad\;\;\| \\ H-C-NHR \end{array}$$

XIV.



$$\begin{array}{r} H-C-COOC_2H_5 \\ \| \qquad\qquad \\ RHN-C-H \qquad\qquad \end{array}$$

XV.

Erlenmeyer[2] has shown that ethyl formate can be condensed with hippuric ethyl ester by means of sodium ethylate to the sodium salt of oxymethylenehippuric ester. We have prepared this salt and find that it condenses very smoothly with pseudoethylthiourea, giving 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine.

We, furthermore, have condensed ethyl formate with phthalimidoethylacetate to the sodium salt of formylphthalimidoethylacetate. We find that this salt condenses with pseudoethylthiourea with the formation of 2-ethylmercapto-5-phthalimido-6-oxypyrimidine, and an intermediate acrylic acid.

The two above pyrimidines show a most striking behavior towards alkali. 2-Ethylmercapto-5-benzoylamino-6-oxypyrimidine dissolves in alkali and is precipitated unaltered by acids, while, on the other hand, the analogous 2-ethylmercapto-5-phthalimido-6-oxypyrimidine is converted under the same conditions into the corresponding pseudoureaphthalimidoacrylic acid.[3]

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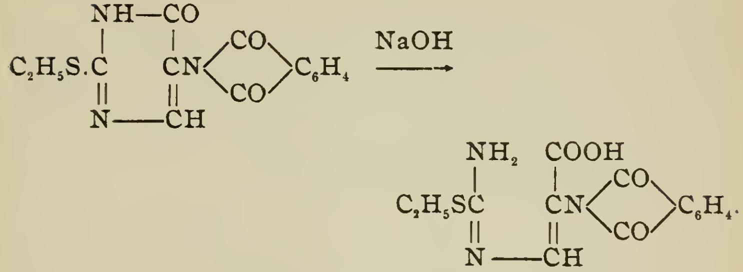
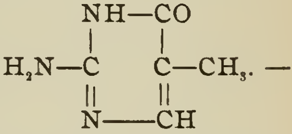
[1] Ber. d. chem. Ges., **25**, 1052.

[2] *Ibid.*, **36**, 3769.

[3] Since the above was written we have found that 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine is converted by alkali into the sodium salt of the corresponding pseudoureabenzoylaminoacrylic acid. We have not succeeded in isolating the free acid.



EXPERIMENTAL PART.

2-Amino-5-methyl-6-oxypyrimidine, 

$$\begin{array}{lcl} & \mathrm{NH}-\mathrm{CO} & \\ & | \qquad | & \\ \mathrm{H_2N}-\mathrm{C} & & \mathrm{C}-\mathrm{CH_3}. \\ & \| \qquad \| & \\ & \mathrm{N}-\mathrm{CH} & \end{array}$$

— Seventy-two grams of guanidine carbonate were dissolved in the least possible quantity of cold water and mixed with 54 grams of barium hydroxide dissolved in 400 cc. of water. To this solution, filtered clear from the precipitated barium carbonate, 283 grams of crude sodium formylethylpropionate were added. After standing at ordinary temperature for about eight hours the clear solution was divided into two equal parts. One part was heated on the steam-bath for about half an hour and then neutralized with dilute sulphuric acid. A brown precipitate separated immediately and was filtered off and saved (see *trans* acid). The clear solution that remained was evaporated to dryness, then redissolved in a little warm water, and filtered from a small amount of insoluble material that was present. The pyrimidine base was then precipitated with phosphotungstic acid, the tungstic acid precipitate decomposed with barium hydroxide, and the excess of barium hydroxide removed in the usual way with carbon dioxide. On concentrating the solution that remained, and cooling, the base separated in the form of stout prisms and melted with effervescence at 320° to 321°.

The second part of the original solution was allowed to stand at ordinary temperature for two weeks. It was then neutralized with dilute sulphuric acid as before. An insoluble brown precipitate was obtained as in the first part. After filtering off this insoluble precipitate we precipitated the pyrimidine base with mercuric chloride instead of phosphotungstic acid. The mercury was removed from the precipitate with hydrogen sulphide and then the base allowed to crystallize from the concentrated solution.

The yield of pure base by the two different methods of treatment was about equal (4 grams), showing that long standing does not increase to any extent the yield. The same observation was made by Wheeler and Johnson[1] in their preparation of isocytosine or 2-amino-6-oxypyrimidine.

2-Amido-5-methyl-6-oxypyrimidine crystallized from hot water in two distinct crystalline forms, stout prisms, and long, slender, needle-like prisms. It melts at 320° to 321° with violent effervescence. It does not contain water of crystallization. One hundred parts of water dissolve 0.43 part base at 25° C. A nitrogen determination gave:

	Calculated for $C_5H_7ON_3$.	Found. I.	II.
N	33.60	33.68	33.91

The base was not hydrolyzed to thymine after heating in a sealed tube with 25 per cent sulphuric acid for five hours.

In a second condensation we modified our experiment in the following manner: After adding the sodium formylethylpropionate to the guanidine solution, we added a molecular proportion of sodium hydroxide (29 grams). The alkaline solution was then allowed to stand at a temperature of 40° to 50° for about ten hours, and then heated on the steam-bath for three hours. The solution was then divided into two equal parts and one part neutralized with acetic acid, the other with dilute sulphuric acid. An immediate precipitate of the *trans* acid resulted in both cases. The weight of insoluble acid obtained here was 12.2 grams.

The two filtrates were combined and precipitated with an excess of mercuric chloride. The mercury was removed in the usual way with hydrogen sulphide and the filtrate concentrated. On cooling the concentrated solution we obtained a mass of needle-shaped prisms mixed with stout prisms. Some of these needle-formed prisms melted at 319° to 320° to a clear oil, followed by a slow effervescence. That this body was not the same product as we obtained in our first condensation was shown by the fact that when it was mixed with the free pyrimidine the melting-point was lowered to 308°–310° (see *cis* acid). The yield of this crystalline product was 18.2 grams.

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[1] *Loc. cit.*

Behavior with Alkali.—The base dissolves very readily in the cold in both dilute (2 per cent) and strong (9 per cent) solutions of sodium hydroxide, and is precipitated unaltered when the alkaline solution is neutralized with carbon dioxide or dilute sulphuric acid. It separates in the form of needle-formed prisms and melts at 320° to 321° with violent effervescence. In appearance this crystalline form of the base resembles very much that of the *cis* acid. That the ring is not opened by the treatment with alkali is shown by the fact that when this body was mixed with the *cis* acid the melting-point was lowered to 307°. Furthermore, a nitrogen determination gave:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.90

The Hydrochloride.—Some of the base was dissolved in concentrated hydrochloric acid and the solution concentrated in a vacuum. The hydrochloride separated in stout prisms. A chlorine determination agreed with the calculated for monohydrochloride:

	Calculated for $C_5H_7ON_3.HCl$.	Found.
Cl	21.98	21.73

The Picrate.—The picrate separated immediately from water in yellow, microscopic crystals. They were practically insoluble in boiling alcohol and water. After prolonged boiling with water the insoluble picrate was filtered off and analyzed for nitrogen:

	Calculated for $C_5H_7ON_3.C_6H_3O_7N_3$.	Found.
N	23.73	23.92

The Sulphate.—The sulphate crystallized from water in the form of flattened prisms or plates. A sulphur determination agreed with the calculated for an acid salt. It is interesting to note that Jaeger[1] obtained analogous acid sulphates from the isomeric 2-amido-4-methyl-6-oxypyrimidine, and from 2-amido-4,5-dimethyl-6-oxypyrimidine :

	Calculated for $C_5H_7ON_3.H_2SO_4$.	Found.
S	14.34	14.62

Platinum Chloride Double Salts.—Two characteristic platinum chloride double salts were obtained. The first was prepared by adding hydrogen platinic chloride to a cold, dilute hydrochloric acid solution of the base. It analyzed for a salt with 4 molecules of water of crystallization :

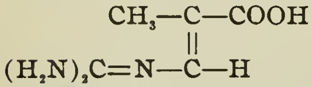
	Calculated for $(C_5H_7ON_3.HCl)_2PtCl_4.4H_2O$.	Found. I.	Found. II.
Pt	26.56	26.51	26.61

When hydrogen platinic chloride was added to a hot hydrochloric acid solution of the base and then the solution allowed to cool slowly, the platinum salt separated in thick tables and melted at 254° to 255°. A water determination and an analysis for platinum agreed with the calculated for a double platinum salt containing two molecules of water of crystallization :

0.1995 gram salt lost 0.0106 gram H_2O at 120° to 130° C.

	Calculated for $(C_5H_7ON_3.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.99	27.76
H_2O	5.17	5.30

Trans-α-Methyl-β-guanidineacrylic Acid,



$$\begin{array}{l} \qquad\quad CH_3—C—COOH \\ \qquad\qquad\quad \| \\ (H_2N)_2C{=}N—C—H \end{array}$$

.—This acid was always obtained in the condensation described above, when we neutralized the alkaline solution, preliminary to precipitating the pyrimidine base with mercuric chloride. It separated as an amorphous brown precipitate. One of the most characteristic physical properties that distinguished this acid from its *cis* modification and the pyrimidine was its insolubility in water. One hundred parts of water dissolve 0.08 part acid at 25° C. It crystallized from boiling water in poorly developed prisms, and melted according to the rate of heating from 329° to 332° with violent effervescence. It possesses both acid and basic properties. A nitrogen determination gave:

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[1] Ann. Chem. (Liebig), 262, 371.

	Calculated for $C_5H_9O_2N_3$.	Found.
N	29.37	29.32

In our second condensation the *trans* acid came down less pure and was mixed with a considerable amount of stout prisms. These were separated by boiling with water. After filtering and cooling, the prisms separated again and melted at 320° to 321° with effervescence. That this was the pyrimidine base was shown by the fact that when mixed with the pure pyrimidine the melting-point was not lowered. The *trans* acid was not changed to the *cis* modification or the pyrimidine after boiling in water for six hours. A nitrogen determination in the above pyrimidine, melting at 320° to 321°, gave:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.68

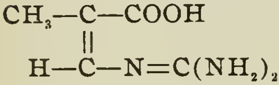
Behavior with 9 Per Cent Sodium Hydroxide.—When the *trans* acid was dissolved either in the cold or warm sodium hydroxide solution, and the solution neutralized with carbon dioxide it separated in the form of stout prisms and melted at 320° to 321° with violent effervescence. That this was the pyrimidine base was confirmed by a nitrogen determination:

	Calculated for		Found.
	$C_5H_7ON_3$.	$C_5H_9O_2N_3$.	
N	33.60	29.37	33.52

The formation of the pyrimidine from the *trans* acid was furthermore confirmed by the formation and analysis of its platinum chloride salt. It separated in the form of stout prisms and melted at 254° to 255°. When mixed with the double salt previously described as melting at 254° to 255° the melting-point was not lowered. A platinum determination gave:

	Calculated for $(C_5H_7ON_3.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.99	27.93

Behavior with 2 Per Cent Sodium Hydroxide.—Some of the *trans* acid melting at 331° was dissolved in the cold, dilute sodium hydroxide solution. On neutralizing with dilute sulphuric acid it separated again as a brown, poorly crystallized precipitate. It was extremely insoluble in water and melted at 330° to 332° with violent effervescence. The *trans* acid was precipitated again unaltered after this treatment with dilute alkali. When mixed with the pure analyzed acid the melting-point was not lowered. This experiment is of interest because it enabled us to determine the *cis* and *trans* forms of our acid. The isomeric modification could not be precipitated unaltered from an alkaline solution.



$$\begin{array}{l} CH_3—C—COOH \\ \quad\;\; \| \\ \;H—C—N{=}C(NH_2)_2 \end{array}$$

Cis-α-Methyl-β-guanidineacrylic Acid, .—This acid was obtained in our second condensation when we precipitated with mercuric chloride to obtain the pyrimidine base. After removing the mercury from the precipitate with hydrogen sulphide and concentrating the solution it separated with the pyrimidine base in slender, needle-like prisms. It was obtained pure by recrystallizing from hot water. It was approximately about twice as soluble in water as the pyrimidine. One hundred parts of water dissolve 0.84 part acid at 25°. The most noticeable physical property which this acid possesses is its behavior on melting. It melts at 319° to 320° to a clear oil, followed by a slight effervescence and slow decomposition. A nitrogen determination gave :

	Calculated for $C_5H_9O_2N_3$.	Found. I.	II.
N	29.37	29.05	29.6

In order to be certain that we were dealing here with a second modification of the guanidineacrylic acid, and not with a modification of our pyrimidine containing water of crystallization, some of the acid was heated for one hour at 115° to 120°, and again at 140° for one hour. The body lost no weight by this treatment, thus confirming our assumption that we had in hand an isomeric acid.

Behavior with 9 Per Cent Sodium Hydroxide.—The *cis* acid dissolved immediately in the sodium hydroxide solution. When the alkaline solution was neutralized with carbon dioxide or with dilute hydrochloric acid an asbestos-like precipitate of needle-like prisms were obtained. They melted at 319° to 321° with effervescence. When mixed with the pyrimidine (m. p. 320°) the melting-point was not lowered. When mixed with the *cis* acid (m. p. 319° to 320°) the melting-point was lowered to from 302° to 303°. That the *cis* acid had been converted into the pyrimidine was confirmed by a nitrogen determination:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.23

Behavior with 2 Per Cent Sodium Hydroxide.—The *cis* acid that was used in this experiment melted sharply at 320° to a clear oil and analyzed for 29.05 per cent of nitrogen, calculated 29.37 per cent. It dissolved immediately in the cold, dilute sodium hydroxide solution. When the alkaline solution was neutralized with carbon dioxide or sulphuric acid the base was precipitated in needle-like prisms melting at 320° with effervescence. A nitrogen determination agreed with the calculated for the pyrimidine:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.43

Acetic acid also precipitated from an alkaline solution of the *cis* acid, the pyrimidine melting at 320°.

Condensation of Ethyl Formate with Phthalimidoethylacetate.—This condensation was effected by suspending the phthalimidoethylacetate in benzene or ether with the calculated amount of sodium and adding slowly the ethyl formate. The condensation was not smooth, and after standing for several hours, with occasional shaking, much phthalimidoethylacetate remained unaltered. From 50 grams of phthalimidoethylacetate about 50 grams of crude sodium salt were obtained.

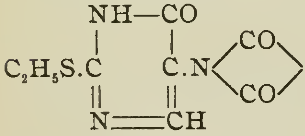
This sodium salt is exceedingly unstable in aqueous solution. Some of the salt was dissolved in water and then filtered. When this clear salt solution was allowed to stand for several hours at ordinary temperature it gradually deposited a crystalline solid. This crystallized from alcohol in needle-like prisms and melted at 111°. It proved to be unaltered phthalimidoethylacetate. When the filtered solution was acidified with hydrochloric acid no further precipitation took place.

On the other hand, when a solution of the sodium salt was immediately acidified with hydrochloric acid a semisolid precipitate was obtained. It was insoluble in hot water. It dissolved in cold alcohol with the exception of a small amount of white, crystalline material. This insoluble product crystallized from hot alcohol in needles and melted at 193° to 194°. It was soluble in alkali to a yellow solution. This body was identified as 4-oxyisoquinoline-3-carboxylic ethyl ester, which was obtained by Gabriel and Colman[1] by heating phthalimidoethylacetate with sodium ethylate and alcohol at 100°. A nitrogen determination gave:

	Calculated for $C_{12}H_{11}O_4N$.	Found.
N	6.00	6.21

When the above alcoholic extract was evaporated to dryness a thick syrup was obtained which immediately solidified on cooling. It crystallized from alcohol in prisms and melted at 111° to 112°. It was identified as phthalimidoethylacetate.

2-Ethylmercapto-5-phthalimido-6-oxypyrimidine,



C_6H_4.—This pyrimidine was obtained by condensing pseudoethylthiourea in aqueous solution with the sodium salt of formylphthalimidoethylacetate. Six and two-tenths grams of the crude salt were treated with 160 cc. of water and filtered from the unaltered phthalimidoethylacetate. To the clear solution was then added an aqueous solution of the pseudourea, that was prepared by mixing a solution of 36 grams of the hydrobromide with 11 grams of potassium hydroxide. The resulting mixture was then allowed to stand at ordinary temperature for one hour, and then heated on the steam-bath. Mercaptan was evolved in large amount, and on prolonged heating the solution assumed a dark-green color. A crystalline precipitate finally began to separate from the hot solution when the mixture was removed from the bath and allowed to cool. This crystalline body proved to be phthalimidoethylacetate. On acidifying the solution with sulphuric acid a thick, gummy precipitate was obtained, which was purified by boiling with water and animal charcoal. It crystallized from alcohol in rhombic plates and melted at 230° to 231° to a yellow oil. It gave a strong test for sulphur. A nitrogen determination gave :

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[1] Ber. d. chem. Ges., 33, 983.

	Calculated for $C_{14}H_{11}O_3N_3S$.	Found.
N	13.95	14.3

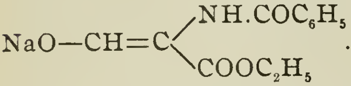
When the above pyrimidine was dissolved in alkali and then acidified with dilute hydrochloric or sulphuric acid a white, crystalline precipitate was immediately obtained. It crystallized from 50 per cent alcohol and melted with violent effervescence at 130° to 131°, then solidified again in the hot bath, and did not melt again until 229° to a clear, yellow oil. It gave a strong test for sulphur. A nitrogen determination agreed with the calculated for α-phthalimido-β-pseudoethylthioureaacrylic acid,

$$C_6H_4(CO)_2N—C(COOH)=CH.N=C(SC_2H_5)—NH_2 :$$

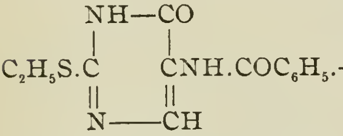
	Calculated for $C_{14}H_{13}O_4N_3S$.	Found.
N	13.16	13.26

This same acid was obtained in the above condensation when the acid filtrates were allowed to stand. It separated in small prisms and was purified by crystallizing from alcohol. When the acid was heated above its melting-point in an oil-bath it immediately decomposed with loss of a molecule of water, giving the pyrimidine derivative melting at 231°.

When mixed with the pyrimidine the melting-point was not lowered.

Sodium Salt of Oxymethylenehippuric Ethyl Ester,  $NaO{-}CH{=}C\begin{matrix}\diagup NH.COC_6H_5\\ \diagdown COOC_2H_5\end{matrix}$.—This salt was used by Erlenmeyer[1] in his synthesis of serine and cystine. He gives no directions for preparing the salt, but states that he obtained it by condensing ethyl formate with hippuric ethyl ester in presence of sodium ethylate.

We have prepared the salt by condensing hippuric ethyl ester with ethyl formate in benzene in the presence of metallic sodium. The condensation is very slow. From 25 grams of hippuric ester we obtained 35 grams of the crude salt.

2-Ethylmercapto-5-benzoylamino-6-oxypyrimidine,  $\begin{array}{lcl} & NH{-}CO & \\ & | \quad\;\; | & \\ C_2H_5S.C & & CNH.COC_6H_5 \\ & \| \quad\;\; \| & \\ & N{-}{-}CH & \end{array}$.—Thirty-five grams of the above sodium salt were dissolved in cold water and combined with an aqueous solution of pseudoethylthiourea. Only 0.5 molecular proportion of pseudourea was used in this reaction, or 13 grams of the hydrobromide, which were neutralized with 4 grams of potassium hydroxide. The mixture was allowed to stand at ordinary temperature for forty-eight hours. No odor of mercaptan was noticeable. When the mixture was examined a large amount of crystalline material had separated from the aqueous solution. This crystallized from alcohol in needles and melted at 238° to 239° to a yellow oil. It gave a strong test for sulphur and did not decompose when heated to 260°. A nitrogen determination gave:

	Calculated for $C_{13}H_{13}O_2N_3S$.	Found.
N	15.27	15.50

The pyrimidine was soluble in alkali and was precipitated unaltered by hydrochloric acid.

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[1] Ber. d. chem. Ges., **36**, 3769; **35**, 2720.

When the alcoholic filtrates from the above purification were combined and evaporated to dryness an oil was obtained which finally solidified. It was identified as unaltered hippuric ester.

More of the above pyrimidine was obtained by acidifying the original solution after filtering off the crystalline material that had separated. It was precipitated as a semisolid, which quickly solidified on cooling. It crystallized from alcohol in needles and melted at 238° to 239°.

NEW HAVEN, CONN., Feb. 24, 1904.

Contributions from the New York Agricultural Experiment Station.

VIII.—CHEMICAL CHANGES IN THE SOURING OF MILK.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

In the ordinary souring of milk two phenomena are familiar: First, the formation of acid, resulting in giving milk a sour taste and a characteristic odor, and, second, the curdling or coagulation of the milk-casein. The formation of lactic acid in the souring of milk from milk-sugar by means of acid-forming organisms has been well known for years, but the character of the action causing coagulation of milk-casein has not been satisfactorily established, though explained in various ways.

Among the explanations that have been offered to indicate what takes place when an acid precipitates milk-casein, we will call attention to two. The first explanation was offered by Scheele in 1780, who was the pioneer in the study of lactic acid. He expressed the view that the precipitate formed by treating milk with an acid is a compound produced by the union of the acid with milk-casein. In 1865, Millon and Commaille[1] carried on some experiments which led them to the same view. In 1893 Timpe[2] made a study of the souring of milk and stated that a given amount of casein unites with a definite quantity of lactic acid to form a definite chemical compound. Owing to the variation in views expressed by different workers, Hammarsten[1] took up the question and concluded as a result of his work that there was no ground for believing that a chemical combination takes place between casein and the acid used to precipitate it. He based his statement mainly on the fact that by rubbing for several days in a mortar with different portions of water, a precipitate formed by casein with an acid, he was able to remove the acid so completely that the remaining precipitate gave no test for the acid. With the more recent knowledge we have of the looser forms of chemical combination common to proteids and the tendency of such compounds to dissociate under conditions less severe than those used by Hammarsten, his work cannot be regarded as settling the question in such an absolute manner as he indicates. According to Hammarsten,[2] milk-casein contains calcium phosphate in combination, and the treatment with acid removes the calcium phosphate, which results in precipitating casein. This view in somewhat modified forms has been held by Eugling,[3] Schaffer,[4] and Söldner.[5]

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[1] Compt. rend., 59, 301 (1865).

[2] Arch. Hyg., 18, 1 (1893).

In this JOURNAL (**28**, 424–430 (1902)) we called attention, in a preliminary way, to the fact that we had isolated two different compounds formed by casein when treated with lactic acid, one of which we were led to regard as casein monolactate and the other as casein dilactate. Both compounds are insoluble in water. The monolactate is completely soluble at about 55° C. in a 5 per cent solution of sodium chloride, while the dilactate is practically insoluble in this solvent. It appears that Hammarsten really prepared these compounds but did not recognize what they were or their relations to each other. He says:[6] "When we carefully precipitate a very dilute solution of casein with a very dilute acid, there is formed a loose precipitate, which dissolves completely in sodium chloride to an opalescent solution." He adds that when too much acid is used a precipitate is formed that is insoluble in sodium chloride solution.

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[1] Maly Jahresber. Thierchemie, **7**, 160 (1877).

[2] *Ibid.*, **4**, 135 (1874).

[3] Landw. Versuchs.-Stat., **31**, 392 (1885).

[4] Landw. Jahrb. d. Schweiz, **1**, 33 (1887).

[5] Landw. Versuchs.-Stat., **35**, 351 (1889).

[6] Maly Jahresber. Thierchemie, **7**, 163 (1877).

We are still engaged in making a more complete study of the chemical relations of acids to casein, the final results of which will be published later. By our further study we have been able to prepare these compounds under more complete control. Some of our more recent results indicate that it may be necessary to modify to some extent the interpretation of our previous results. While many facts favor the view that there is a direct combination between the proteid and acids, other facts are not in full harmony with this position. We hope to obtain data in the near future which will furnish us a satisfactory basis for reaching definite settled conclusions in regard to this question, which has been so long a troublesome and difficult problem. Until our present interpretation of our results has been clearly shown to be inconsistent with the facts previously ascertained by us, we shall continue tentatively to speak of the compounds in question as mono- and di-salts of casein and paracasein.

It is our purpose in this paper to present the results of some recent work done to show the amounts of the casein monolactate and dilactate formed in the usual souring of milk, together with the results of a simultaneous study of some of the conditions under which the sugar in milk is changed into lactic acid.

In one set of experiments made in our study, we placed some fresh separator skim-milk in an Erlenmeyer flask, stoppered with a plug of cotton. This was allowed to stand at room temperature, and samples were taken from this flask for examination from time to time. In the first experiment the room temperature varied from 18° to 24° C.; in the second from 21° to 27° C. In another set of experiments we used 3000 cc. of pasteurized separator skim-milk, to which had been added 50 cc. of sour milk to hasten the souring. We placed in each of 14 cotton-stoppered flasks 100 cc. of this milk and allowed one lot (No. 3) to stand at a temperature of 15°.5 to 21° C., and another lot (No. 4) at 21° to 27° C. In these experiments (3 and 4) we used the contents of one flask

Table Showing Chemical Changes in the Souring of Milk.

No. of experiment.	Age of milk when analyzed. Hours.	Amount of milk-sugar in milk. Per cent.	Amount of milk-sugar changed. Per cent.	Amount of lactic acid in milk. Per cent.	Proportion of sugar in milk changed. Per cent.	Nitrogen in milk in soluble form. Per cent.	Casein in form of monolactate. Per cent.	
1	Fresh	5.15	....	....	....	....	....	
2	"	5.58	....	....	....	....	....	
3	"	5.08	....	0.187	....	....	....	
4	"	5.08	....	0.187	....	....	....	
1	8	4.53	0.62	....	12.04	....	....	
2	8	5.25	0.33	....	5.91	....	....	
3	8	4.53	0.55	0.011[1]	10.83	....	....	
4	8	4.32	0.76	0.081[1]	14.96	....	....	
1	24	4.25	0.90	....	17.48	....	....	
2	24	4.42	1.16	....	20.80	21.19	12.70	Coagulated
3	24	4.00	1.08	0.506[1]	21.26	....	....	
4	24	3.79	1.29	0.776[1]	25.40	....	....	Coagulated
3	26	3.92	1.16	0.596[1]	28.43	....	....	Coagulated
1	29½	3.88	1.27	....	24.66	17.44	14.43	Coagulated
1	32	3.71	1.44	....	28.00	22.61	13.18	
2	32	4.20	1.38	....	24.73	22.63	11.50	
3	32	3.86	1.22	0.740[1]	24.00	....	....	
4	32	3.76	1.32	0.848[1]	26.00	....	....	

[1] Amount of lactic acid less the amount of acid in the fresh milk.

Table Showing Chemical Changes in the Souring of Milk (Continued).

No. of experiment.	Age of milk when analyzed.	Amount of milk-sugar in milk.	Amount of milk-sugar changed.	Amount of lactic acid in milk.	Proportion of sugar in milk changed.	Nitrogen in milk in soluble form.	Casein in form of monolactate.
	Hours.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	48	3.70	1.45	....	28.10	22.80	10.20
2	48	4.18	1.40	....	25.10	21.19	8.61
3	48	3.79	1.29	0.821[1]	25.40	....	....
4	48	3.76	1.32	0.848[1]	26.00	....	....
1	72	3.65	1.50	....	29.13	24.14	8.00
2	72	4.13	1.45	....	26.00	21.38	8.61
3	72	3.76	1.32	0.839[1]	26.00	....	....
4	72	3.72	1.36	0.857[1]	26.77	...	....
1	96	3.66	1.49	....	28.93	23.95	6.70
2	96	4.07	1.51	....	27.06	22.87	6.00
3	96	3.70	1.38	0.875[1]	27.16	....	....
4	96	3.69	1.39	0.884[1]	27.36	....	....
2	120	4.07	1.51	....	27.06	22.68	5.74
3	120	3.62	1.46	0.893[1]	28.74	....	....
4	120	3.64	1.44	0.884[1]	28.35	....	....

[1] Amount of lactic acid less the amount of acid in the fresh milk.

for making an analysis at each stated period of time, no flask being opened until its contents were used. The results of these experiments are given in the table on preceding pages.

Decrease of Milk-sugar.

In all cases the loss of milk-sugar increased quite rapidly for thirty-two hours, after which additional change was slow and small. In seventy-two to one hundred and twenty hours the maximum loss was reached; in experiment No. 1 no further change of milk-sugar occurred after seventy-two hours, and in No. 2 none after ninety-six hours. Of course, at temperatures somewhat higher, less time would be required for the transformation of the same amount of milk-sugar. Averaging our results, we find that about 11 per cent of the sugar present in the milk at the start had disappeared in eight hours, 21 per cent in twenty-four hours, 25.5 per cent in thirty-two hours, 26 per cent in forty-eight hours, 27 per cent in seventy-two hours, and 27.6 per cent in ninety-six hours.

Amount of Lactic Acid Formed.

The maximum amount of lactic acid formed, calculated as lactic acid, was about 0.90 per cent, which is equivalent to about 62 per cent of the milk-sugar that disappeared. It is customary to represent in the following manner the reaction by which milk-sugar is converted into lactic acid:

$$C_{12}H_{22}O_{11} + H_2O = 4C_3H_6O_3.$$

According to this expression, all the milk-sugar is converted into lactic acid, weight for weight. While this equation expresses the most prominent chemical reaction that occurs, it certainly fails to give anything like a complete or accurate statement of the entire chemical reaction. In detail, our average results are as follows: In twenty-four hours, 40 per cent of the milk-sugar that had disappeared formed acid, largely lactic; in thirty-two hours, 58.5 per cent; in forty-eight hours, 64 per cent; in seventy-two hours, 63.3 per cent; in ninety-six hours, 63.5 per cent; in one hundred and twenty hours, 61.3 per cent.

As shown by Kayser,[1] there may be present in addition to lactic acid, as the products of the decomposition of milk-sugar by lactic-acid forming organisms, carbon dioxide gas, formic acid, acetic acid, acetone, and alcohol. Mayer[2] has found that under the most favorable conditions we may possibly be able to get as much as 83.9 parts of lactic acid from 100 parts of milk-sugar, but the conditions used by him are not such as normally exist in milk. The presence of alcohol, volatile fatty acids, and gases among the lactic-acid fermentation-products has also been shown by Leichmann,[3] and acetone by Jaksch.[4] The quantity of acid formed is, according to Emmerling,[5] dependent upon a variety of conditions, among which the following may be mentioned: The kind of organism; the reaction of the material, a neutral reaction being favorable; the presence or absence of air, the presence of air favoring the formation of more of the volatile acids; the conditions of nutrition, of temperature, and of the presence or absence of certain substances.

According to Timpe,[6] for example, one of the lactic acid organisms studied by him is checked in its growth by 0.04 per cent of free lactic acid. However, the growth is not checked so long as there are substances present with which the acid can unite. We have such substances in milk. Using as a basis the figures given by Söldner,[7] the inorganic compounds in 100 grams of milk would unite with 0.3938 gram of lactic acid. Timpe found that 100 grams of milk-casein neutralize 8.415 grams of lactic acid. The milk-casein in 100 grams of milk containing 2.5 per cent of casein would therefore neutralize 0.2104 gram of lactic acid. Thus, the total amount of lactic acid neutralized by 100 grams of ordinary milk would be 0.604 per cent, and this was about the amount of acid found by him in milk that had soured in the usual way. In his experience the maximum amount of acid is reached in about fifty hours at ordinary temperatures. Our results are somewhat higher than those of Timpe. We find as our maximum somewhat more lactic acid, which is nearly all formed in forty-eight to seventy-two hours. There will, of course, be a variation in different milks dependent upon the amount of casein and inorganic salts, other conditions being uniform. Richet[1] states that he has found as much as 1.6 per cent of lactic acid in sour milk, but this figure is so much higher than any one else has found that there must be some error in his method of determination. Hueppe[2] finds the amount of lactic acid formed in sour milk about 0.8 per cent, which is in close agreement with our results.

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[1] Ann. Past, 8, 737 (1894).

[1] Centrbl. Bakt., **12**, 99 (1892).

[3] *Ibid.*, **16**, 826 (1894).

[4] Ber. d. chem. Ges., **19**, 781, R.

[5] Die Zersetzung stickstofffreier organischen Substanzen durch Bakterien, p. 34.

[6] Arch. Hyg., **18**, 1 (1893).

[7] Landw. Versuchs.-Stat., **35**, 351 (1889).

Relation of Coagulation of Milk to Amount of Acid.

In the case of experiment No. 3, the milk was found completely coagulated, that is, solidified in a mass, in twenty-six hours, when the amount of acid had reached about 0.6 per cent. In experiment No. 4, the time of coagulation was twenty-four hours and the percentage of acid was nearly 0.8. The milk in No. 2 had just coagulated at the end of twenty-four hours. In the case of experiments 1 and 4, the milk coagulated during the night and our observation was made in the morning, just how long after coagulation we do not know. Under the ordinary conditions of souring, we can expect, according to these results, that milk will coagulate when the total acid reaches about 0.8 or 0.9 per cent, as indicated by titration with standard alkali and phenolphthalein as indicator. Deducting the amount of the original titration of the fresh milk and calling the rest lactic acid, we have coagulation taking place when the lactic acid reaches 0.6 to 0.7 per cent. In producing this amount of lactic acid about 1.3 per cent of milk-sugar disappears, which is about 25 per cent of the sugar originally present in the milk.

Soluble Nitrogen Compounds in Sour Milk.

The soluble nitrogen compounds in the sour milk amounted to about 22 per cent of the nitrogen in the milk. This is practically all accounted for by the milk-albumin. The constancy of the amount of soluble nitrogen also suggests that it was present mostly, if not entirely, as milk-albumin.

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[1] Compt. rend., **86**, 550 (1878).

[2] Mittheil. a. d. Gesundh., **2**, 309 (1884).

Formation of Casein Monolactate and Casein Dilactate in Milk Coagulated by Ordinary Souring.

When the milk was first visibly coagulated the amount of casein in the form of monolactate was 13 to 14 per cent of the casein in the milk, and the amount of casein dilactate was 86 to 87 per cent of the casein in the milk. As the milk grew more acid, the monolactate gradually passed into the dilactate. The minute amount of monolactate apparently present at the time the experiment was stopped is due to a slight solubility of dilactate in a 5 per cent solution of sodium chloride. When milk coagulates by souring in the usual way, the casein is nearly all in the form of dilactate at the time the milk has set in a solid mass.

It was desired to determine the amount of casein monolactate in milk before the milk visibly coagulates. For studying this point, some milk was set aside one day at 5 P. M. and the next forenoon was warmed to about 40° C., when casein monolactate separated from the milk. In this case 65 per cent of the casein was in the form of monolactate, while no dilactate was present.

Separation of Casein, Casein Monolactate, and Casein Dilactate.

The method employed by us in separating casein, casein monolactate, and casein dilactate, when they occur together in milk, is as follows : The milk is heated to 40° C. and the monolactate separates as a precipitate. When only casein and casein monolactate are present, simple filtration with washing serves to separate them. When the two lactates are present in the coagulum formed after heating, they are removed from other milk constituents by filtration, and the monolactate is dissolved in a 5 per cent solution of sodium chloride at about 55° C., after which the two compounds are separated by filtration.

Summary.

1. The purpose of the work described in this paper was to study the chemical changes that take place in the ordinary souring of milk, especially those changes that affect the decomposition of milk-sugar, the formation of lactic acid, and the production of casein monolactate and casein dilactate.

2. The loss of milk-sugar increased quite rapidly for thirty-two hours at room temperatures (18° to 27° C.), after which the change was small and ceased in seventy-two to ninety-six hours, when the maximum loss of milk-sugar was reached, about 1.50 per cent, equivalent to about 28 per cent of the sugar originally present in the milk.

3. The maximum amount of lactic acid formed was about 0.9 per cent, which is equivalent to about 62 per cent of the milk-sugar that disappeared.

4. At the temperature used, the milk coagulated in twenty-four to twenty-nine and a half hours, when the percentage of total acid shown by titration had reached 0.6 to 0.7.

5. When the milk was first visibly coagulated, 13 to 14 per cent of the casein was in the form of monolactate and 86 to 87 per cent was in the form of dilactate. With further increase of acid in the milk, the monolactate passes into the dilactate.

GENEVA, N. Y., March 1, 1904.

Contributions from the New York Agricultural Experiment Station.

IX.—A STUDY OF THE ARTIFICIAL DIGESTION OF SOME COMPOUNDS OF CASEIN AND PARACASEIN CONTAINED IN COTTAGE AND CHEDDAR CHEESE.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

There is a popular belief, which appears to have some foundation in experience, that certain compounds of casein used as food are more digestible than certain compounds of paracasein also used as food. Put into the ordinary mode of expression, it is commonly believed that fresh cottage, or Dutch, cheese is more easily digested than cheddar cheese, especially new cheddar cheese. Cottage cheese, also commonly known as Dutch cheese, is prepared by allowing milk to coagulate by ordinary souring, heating to aid separation of whey, allowing the curd to drain, and then shaping it into balls. When thus prepared, it consists essentially of casein dilactate, holding 70 to 75 per cent of moisture. The coagulation is sometimes aided by adding a small amount of rennet, in which case the cheese is largely paracasein dilactate. Cottage cheese may also be prepared by adding 0.6 per cent of lactic acid or 0.25 per cent of hydrochloric acid to milk, forming in the latter casein dihydrochloride. In new cheddar cheese, the kind that is most commonly made and consumed in America, the nitrogen is largely in the form of paracasein monolactate.

It seemed desirable to ascertain by artificial peptic digestion to what extent laboratory experiments are in harmony with the popular belief referred to. We have worked with the following materials: Paracasein, paracasein monolactate of new cheddar cheese, paracasein dilactate, casein monolactate, casein dilactate (cottage cheese) prepared by normal souring of milk and by direct addition of lactic acid to milk, and casein dihydrochloride. These materials have been treated with varying amounts of pepsin, with and without hydrochloric acid. Some experiments were also made to determine the influence of the fineness of the materials upon the rate of digestion.

(*1*) *Comparison of Digestibility of Paracasein and Paracasein Monolactate without Acid.*

The paracasein used in this experiment was prepared by coagulating fresh milk with rennet extract; it was carefully washed. As the source of paracasein monolactate, we used freshly prepared cheddar cheese in which over 75 per cent of the nitrogen was present in the form of paracasein monolactate. The samples (25 grams) were ground with sand and in each of several bottles there was placed material equivalent to 0.694 gram of nitrogen with 80 cc. of water. The bottles and contents were heated to 100° C. for fifteen minutes to destroy all enzymes and active organisms. After cooling, there were added to each bottle 3 cc. of chloroform and 20 cc. of pepsin solution containing 0.150 gram of Parke Davis & Co.'s aseptic scale pepsin. The bottles were kept at 37° C. and examined at intervals. Enough bottles were prepared in each case so that one bottle was used for each examination, no bottle being opened until analyzed. The analytical results are given in Table I.

These results show that the paracasein failed to digest, while the paracasein monolactate digested quite rapidly when we consider the absence of free acid.

(2) *Comparison of Digestibility of Casein Monolactate and Casein Dilactate without Acid.*

The casein monolactate was prepared by treating 20 pounds of milk with 32.6 grams of lactic acid. On heating at 37° to 40° C., the monolactate separated as a characteristic rubber-like mass. A portion of it was found, on testing, to dissolve completely in a 5 per cent solution of sodium chloride. The casein dilactate was prepared by allowing milk to sour in the usual way for making cottage cheese. These materials, carefully washed, were prepared for digestion as described under (1) preceding, except that in each bottle we used 0.200 gram of pepsin, in place of 0.150 gram, and 1 per cent of chloroform instead of 3 per cent. The amount of nitrogen in the material in each bottle was 0.830 gram. No acid was added to the contents of the bottles. The results are given in Table II.

The casein monolactate digested, in the absence of free acid, somewhat more rapidly than the dilactate. This result we did not anticipate, since it was expected that the compound containing the higher amount of acid would be acted upon more readily by pepsin. In explanation of this behavior, it may be suggested that the acid in the dilactate appears to be in more stable combination than in the monolactate.

(3) *Comparison of the Digestibility of Paracasein Monolactate and Paracasein Dilactate with and without Free Acid.*

The paracasein dilactate was prepared by allowing 20

Table I.—Showing Digestion of Paracasein and Paracasein Monolactate by Pepsin without Free Acid.

Material containing	Per cent of nitrogen in material.	Per cent of nitrogen in form of paracasein monolactate.	Per cent of nitrogen in material in soluble form.	Percentage of nitrogen in material expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
				Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Paracasein	4.11	....	2.43	6.62	6.62	7.06	7.64	6.62
Paracasein monolactate	3.52	75.27	3.98	17.00	22.62	22.91	40.78	45.96

Table II.—Showing Digestion of Casein Monolactate and Casein Dilactate by Pepsin without Acid.

Material.	Percentage of nitrogen in material.	Total nitrogen in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
			In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Casein dilactate	2.34	0.830	8.56	11.81	21.69	22.65	23.37
Casein monolactate	4.15	0.830	14.34	16.51	23.61	26.63	29.64

pounds of milk, mixed with half a pound of sour milk, to stand eight hours at room temperature and then adding 0.5 cc. of rennet extract, after which the mass was allowed to remain until it had become quite acid and was completely coagulated. The monolactate was obtained in the form of new cheddar cheese, in which 66.21 per cent of the nitrogen was in the form of monolactate. These materials were prepared for digestion as described under (1) preceding, except that we used 0.300 gram of pepsin and 1 cc. of chloroform, and in experiments 3 and 4 we used in addition 0.4 per cent of hydrochloric acid.

In studying the data embodied in Table III., we notice the same fact to which attention has already been called, *viz.*, that in the absence of free acid the monolactate undergoes pepsin digestion more rapidly than the dilactate. When, however, free acid is present, the reverse is true, the dilactate digesting more readily than the monolactate. The initial activity of digestion is considerably greater in both cases in the presence of acid. The following explanation is suggested to show why, in the presence of free acid, the dilactate digests more rapidly: The monolactate is first converted into dilactate and thus uses some of the acid, so that less acid is left free to take part in the pepsin digestion.

(*4*) *Comparison of Digestibility of Casein Dilactate and Casein Dihydrochloride with and without Acid.*

The casein dilactate and casein dihydrochloride were prepared by treating milk with 0.6 per cent of lactic acid and 0.2 per cent of hydrochloric acid. The resulting products were washed and prepared for digestion as described in (1) and (3) preceding, except that the materials were not ground with sand and were not heated. In 1 and 2 no free acid was added to the digestion bottles, while in 3 and 4 we used 0.4 per cent of hydrochloric acid (see Table IV., p. 159).

The data in Table IV. show no essential difference in digestibility between the casein dilactate and casein dihydrochloride. This is true both in the absence and presence of free acid. Increased digestibility is caused by free acid, the

Table III.—Showing Digestion of Paracasein Monolactate and Dilactate with and without Acid.

	Material.	Per cent of hydrochloric acid used in digestion.	Total nitrogen in material in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Paracasein monolactate	0	0.710	23.66	27.46	49.72	51.84	62.11
2	" dilactate	0	"	14.23	14.51	24.37	31.83	33.52
3	" monolactate	0.4	"	48.31	56.63	46.77	51.56	57.33
4	" dilactate	0.4	"	67.75	73.35	70.43	67.89	73.39

Table IV.—Showing Digestion of Casein Dilactate and Casein Dihydrochloride with and without Acid.

	Material.	Per cent of hydrochloric acid used in digestion.	Total nitrogen in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Casein dilactate	0	0.730	11.37	17.95	34.25	42.47	49.05
2	" dihydrochloride	0	"	11.65	15.07	31.51	43.42	50.69
3	" dilactate	0.4	"	84.94	84.53	96.58	96.04	96.50
4	" dihydrochloride	0.4	"	83.56	85.90	92.20	94.94	97.27

most marked increase being in the first period (four hours) of digestion.

(5) *Comparison of Digestibility of Cottage Cheese Made from Whole Milk and Skim-milk.*

We desired to test the influence of fat in cottage cheese upon its digestibility. The cheese was prepared in each case by adding 0.2 per cent of hydrochloric acid to the milk used. We thus had casein dihydrochloride as our proteid, containing, in one case, 12.65 per cent of fat and, in the other, 0.62 per cent. The materials were prepared for digestion as described in (4) preceding.

The results in this table indicate that the cheese made from whole milk digested more quickly than the cheese made from skim-milk. This could not be accounted for by saying that the whole milk contained more proteolytic enzyme than the skim-milk, because milk-enzymes, even when present in different quantities, do not appear to have the power of producing such differences of digestion in so short a time. The true explanation probably lies in the fact that the whole-milk cheese was much more porous and loose in texture, owing to the presence of the fat, and so offered a better mechanical condition for the action of the digestive agent. The fat in this case not only failed to impede digestion but indirectly favored it.

(6) *Influence of Mechanical Division upon Digestion of Cheese.*

The mechanical condition or fineness of division of food is known to have a marked influence upon digestion. In testing this point, we prepared fresh cheddar cheese and fresh cottage cheese. The cheddar cheese contained 70.4 per cent of its nitrogen as paracasein monolactate. All the bottles contained the same content of water and 0.4 per cent of hydrochloric acid. In Experiment 1, the cottage cheese was made as fine as possible by grinding with quartz sand, while in 2 the cheese was in the condition in which it is ordinarily consumed. In Experiment 3, the cheddar cheese was ground with sand, in 4 it was chopped about as fine as it would be made

Table V.—Showing Digestion of Cottage Cheese Made from Whole Milk and Skim-milk.

Cheese made from	Per cent of fat in cheese.	Per cent of hydrochloric acid used in digestion.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
			In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Whole milk	12.65	0.4	80.97	87.02	88.23	93.26	93.95
Skim-milk	0.62	0.4	68.00	80.28	89.97	93.09	92.91

Table VI.—Showing Influence of Mechanical Division of Cheese upon Digestion.

	Material.	Total nitrogen in each bottle.	Per cent of hydrochloric acid used in digestion.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Cottage cheese, ground fine	0.772	0.4	78.11	91.20	92.49	90.81	90.42
2	" " not ground	"	"	68.27	75.39	89.90	88.86	97.53
3	Cheddar cheese, ground fine	"	"	63.08	72.80	80.32	76.04	83.28
4	" " chopped fine	"	"	34.07	55.54	65.16	78.50	81.87
5	" " in $\frac{1}{4}$-in. cubes	"	"	18.27	29.92	50.78	64.52	69.17

by ordinary chewing, and in 5 it was cut into cubes about one-quarter of an inch in size. In other respects the materials were prepared for digestion as described in (4) preceding (see Table VI., p. 161).

The difference of digestion between the finely ground cottage cheese and that left in the ordinary condition is not large, and after twenty-four hours nearly disappears. In the case of the cheddar cheese, the difference is very striking. When the cheese was ground fine, about twice as much was digested in four hours as when it was chopped fine, and about three and one-half times as much as when cut into quarter-inch cubes. The cottage cheese in its ordinary condition digested more rapidly than the cheddar cheese ground fine.

(7) *Influence of Increasing Amounts of Acid upon Digestion of Cheese.*

In normal gastric digestion in animals, the acid used is secreted gradually and not all poured into the stomach at the start. In order that the conditions of our work might in this respect more nearly approximate normal digestion, we prepared for digestion, as described in (6) preceding, some samples of cottage and cheddar cheese, ground with sand, and added to the digesting mass hydrochloric acid at intervals, as follows: At the start, 0.4 per cent of acid; in two hours, 0.1 per cent; in four hours, 0.1 per cent; in eight hours, 0.1 per cent; in twenty-four hours, 0.1 per cent; in forty-eight hours, 0.1 per cent, making in all an addition of 0.9 per cent of hydrochloric acid. The results are given below in comparison with some digestions in which we used 0.4 per cent of acid at the beginning and added none afterwards.

The addition of 0.4 per cent of hydrochloric acid at the beginning of the digestion, followed by an addition of 0.1 per cent two hours after, increased the amount of digested proteid very noticeably at the first examination, four hours after the digestion began. This was true in both cottage and cheddar cheese. As in previous cases, the cottage cheese was more completely digested than the cheddar cheese.

Table VII.—Showing Effect of Increasing Amounts of Acid upon Digestion of Cheese.

	Material.	Total nitrogen in each bottle.	Per cent of hydrochloric acid used in digestion.		Percentage of nitrogen in material in form of water-soluble nitrogen.				
			Added at start.	Added at intervals.	In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Cottage cheese	0.772	0.4	. .	78.11	91.20	92.49	90.81	90.42
2	" "	"	. .	0.9	86.54	93.91	94.56	91.96	93.26
3	Cheddar "	"	0.4	. .	63.08	72.80	80.32	76.04	83.28
4	" "	"	. .	0.9	78.10	75.91	80.97	87.95	90.68

Summary.

1. In the absence of acid, paracasein fails to be digested by pepsin, while paracasein monolactate (the chief nitrogen compound of fresh cheddar cheese), paracasein dilactate, casein monolactate, casein dilactate (cottage or Dutch cheese), and casein dihydrochloride are partially digested. Paracasein monolactate and casein monolactate, in the absence of acid, are digested more than are paracasein dilactate and casein dilactate.

2. In the presence of 0.4 per cent of hydrochloric acid, paracasein dilactate is digested by pepsin more than is paracasein monolactate. Paracasein monolactate and dilactate, and casein monolactate and dilactate, and casein dihydrochloride digest more readily and completely in the presence of free hydrochloric acid than in its absence.

3. Casein dilactate and casein dihydrochloride do not differ in the rapidity and extent to which they are converted into soluble compounds by pepsin.

4. The addition of acid after the beginning of the digestion increases the amount of proteid digested in both cottage and cheddar cheese.

5. Cottage cheese made from whole milk digests more rapidly than that made from skim-milk, owing to the looser texture of the former. Fat in such cases does not impede digestion.

6. The rapidity of digestion is dependent in part upon the fineness of division of the material to be digested. Cottage cheese, as ordinarily consumed, is in a state of finer division than cheddar cheese.

7. Cottage cheese may properly be regarded as more readily digestible than new cheddar cheese for two reasons: First, the casein dilactate, the chief solid constituent of cottage cheese, is more digestible in the presence of free hydrochloric acid than is paracasein monolactate, the principal nitrogenous constituent of new cheddar cheese. Second, cottage cheese is in such a mechanical condition that it admits of easier attack by digestive agents than does new cheddar cheese.

GENEVA, N. Y., March 1, 1904.

Contributions from the Chemical Laboratory of Lehigh University.

VI.—PROPANETRISULPHONIC ACID.

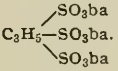
[PRELIMINARY PAPER.]

BY WILLIAM B. SCHOBER.

The only derivatives of propanetrisulphonic acid heretofore described are two barium salts prepared by Schaüfelin[1] in 1868. He treated trichlorhydrine (made by treating dichlorhydrine with phosphorus pentachloride) with a concentrated water solution of neutral potassium sulphite. The reaction, taking place in accordance with the following equation, was complete in twelve hours:

$$C_3H_5Cl_3 + 3K_2SO_3 = C_3H_5(SO_3K)_3 + 3KCl.$$

Owing to the formation of a double salt it was impossible to obtain the potassium propanetrisulphonate free from potassium chloride. He, therefore, treated a solution of the double salt with concentrated sulphuric acid and evaporated it on a water-bath until the odor of hydrochloric acid was no longer perceptible. The residue was extracted with alcohol, boiled with water, and neutralized with barium carbonate. After filtering the hot solution and cooling, a difficultly soluble, white, crystalline powder was deposited. It contained no water of crystallization. A determination for barium and sulphur gave these results:

	Calculated for  $C_3H_5 \begin{cases} SO_3ba \\ SO_3ba. \\ SO_3ba \end{cases}$	Found.
Ba	42.2	42.04
S	19.8	20.2

By diluting the solution he obtained another barium salt, easily soluble, containing water of crystallization. After drying the salt at 150°, a determination for barium gave 41.8 per cent. No other results are recorded.

In order to avoid the difficulty encountered by Schaüfelin, I treated 1,2,3-tribrompropane (tribromhydrine) with ammonium sulphite. The tribromhydrine was prepared by treating allyl iodide with bromine. After being purified it boiled at 216° (uncorr.).

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[1] Ann. Chem. (Liebig), 148, 117.

The ammonium sulphite was made by passing cooled sulphur dioxide, from copper and sulphuric acid, and cooled ammonia, obtained by gently heating concentrated ammonium hydroxide, into 95 per cent alcohol surrounded by a freezing-mixture of ice and salt. I obtained more satisfactory results by employing 95 per cent alcohol than with the absolute. When the latter was used the product was very finely divided and exceedingly difficult to filter.

The tribromhydrine and a saturated solution of 5 molecules of ammonium sulphite were placed in a flask, to which was attached an inverted condenser, and heated on a sand-bath. The substances reacted very slowly. At times, during the progress of the reaction, sulphur dioxide escaped ; in order to avoid this a little ammonium carbonate was added. The heating was continued until all the tribromhydrine had disappeared. The hot, clear solution was filtered and allowed to stand over night. No crystals were deposited. Upon evaporation and cooling, a quantity of ammonium bromide separated out. On further treatment small quantities of ammonium sulphate and more ammonium bromide were obtained. Finally the crystals of what proved to be the ammonium salt of propanetrisulphonic acid were deposited.

The Ammonium Salt, $C_3H_5(SO_3NH_4)_3 + H_2O$.—This salt is very soluble in water with marked lowering of the temperature, difficultly soluble in absolute alcohol, from which it crystallizes in a fine powder composed of minute needles. It has a strong crystallizing force. From a water solution beautiful, brilliant, transparent crystals may be easily obtained. In one experiment a single crystal weighing 12 grams was formed. The salt is efflorescent on long standing; does not melt or char at 360°. A partial analysis gave these results :

I. 0.3419 gram substance, on heating for two hours at 130°, lost 0.0178 gram.

II. 0.1866 gram substance, on heating for one hour at 130°, lost 0.0098 gram.

III. 0.1768 gram substance gave 0.02336 gram N (Kjeldahl-Gunning method).

IV. 0.1454 gram substance, dried at 125°, gave 0.3027 gram $BaSO_4$ (Carius method).

V. 0.1465 gram substance, dried at 125°, gave 0.3058 gram $BaSO_4$ (Carius method).

	Calculated for $C_3H_5(SO_3NH_4)_3 + H_2O$.	Found.	
		I.	II.
H_2O	5.10	5.20	5.25
N	12.53	....	13.2
S	28.62	28.58	28.65

The Barium Salt, $(C_3H_5(SO_3)_3)_2Ba_3 + 5H_2O$.—This salt was made by dissolving the ammonium salt in water and boiling the solution with barium carbonate until the odor of ammonia was no longer perceptible. It is difficultly soluble in hot alcohol, difficultly soluble in water, from which it crystallizes in minute, ill-defined crystals. An analysis gave the following results:

I. 0.3064 gram substance lost 0.0269 gram on heating for two hours at 125°, and gave 0.2001 gram $BaSO_4$.

II. 0.5256 gram substance lost 0.0464 gram on heating one and a half hours at 125°, and gave 0.3448 gram $BaSO_4$.

III. 0.2387 gram substance, dried at 130°, gave 0.0726 gram CO_2 and 0.0366 gram H_2O.

IV. 0.1997 gram substance, dried at 130°, gave 0.0586 gram CO_2 and 0.0284 gram H_2O.

	Calculated for $C_3H_5(SO_3ba)_3 + 5H_2O$.	Found.	
		I.	II.
C	7.40	8.25	8.00
H	1.03	1.70	1.58
H_2O	8.47	8.82	....
Ba	42.24	42.34	....

The investigation of propanetrisulphonic acid and its derivatives will be continued.

South Bethlehem, Pa.,
March 12, 1904.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TRICHLORTRINITROBENZOL.

BY C. LORING JACKSON AND PAUL SHORTT SMITH.

In continuing an extended research, which has been carried on for some years in this laboratory, on the behavior of nitrohalogen derivatives of benzol, it was important to study the trichlortrinitrobenzol discovered by Wing and one of us[1] many years ago. At that time the substance was prepared without difficulty, but more than one man, who had taken up the work later in this laboratory, found it impossible to obtain any of it, although the directions given in the paper cited were followed with the greatest care. It was evident that some condition essential to the preparation of the trichlortrinitrobenzol had been omitted, but even consultation with Dr. Wing failed to show what this condition was. At last, however, Mr. H. A. Carlton discovered that it was necessary to use a return-condenser in converting the trichlordinitrobenzol into trichlortrinitrobenzol, and with this slight change the preparation became once more the easy one described by Wing and one of us. As Mr. Carlton had become interested in another part of the work during his experiments on the manufacture of trichlortrinitrobenzol, we have undertaken the study of this substance.

An alcoholic solution of sodic ethylate reacted vigorously with the trichlortrinitrobenzol, forming even at ordinary temperatures trinitrophloroglucine triethyl ether and trinitrophloroglucine, $C_6(OH)_3(NO_2)_3$. This action therefore resembles in part the behavior of the tribromtrinitrobenzol,[2] which under these conditions gives the same products, but also by a parallel reaction a considerable quantity of tribromnitroresorcine diethyl ether, $C_6Br_3NO_2(OC_2H_5)_2$. No trace of a corresponding replacement of nitro groups was observed by us with the chlorine compound. Trichlordinitrobenzol[3] in the cold formed chlordinitroresorcine diethyl ether, which gives dinitrophloroglucine triethyl ether with a hot solution of sodic ethylate; and the tribromdinitrobenzol[1] gives two bromdinitroresorcine diethyl ethers and dinitrophloroglucine triethyl ether as the principal products in the cold, while, when hot sodic ethylate is used, one of the bromdinitroresorcine diethyl ethers is reduced to dinitroresorcine diethyl ether.

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[1] This JOURNAL, **9**, 354 (1887).

[2] Jackson and Warren: *Ibid.*, **15**, 607 (1893).

[3] Jackson and Lamar: *Ibid.*, **18**, 664 (1896).

With sodic malonic ester one of the atoms of chlorine in the trichlortrinitrobenzol is replaced by the malonic ester radical, but instead of the expected malonic ester the substance isolated by us was a dichlortrinitrophenylacetic ester,

$$C_6Cl_2(NO_2)_3CH_2COOC_2H_5,$$

melting at 130° to 131°, formed by the decomposition of the malonic ester. It is probable that the acetic ester was formed during the distillation with steam used by us in purifying the product, but our attempts to prove this by isolating a pure compound without distillation with steam led to no result. Parallel experiments by H. A. Carlton and one of us[2] with tetrachlordinitrobenzol, however, showed that the trichlordinitrophenylmalonic ester was obtained, when the substance was purified by solution only, whereas the acetic ester was obtained when the mother-liquors were distilled with steam. This, although not conclusive, is strongly in favor of our theory that the acetic ester is formed by the distillation with steam. Tribromtrinitrobenzol,[3] when treated with sodic malonic ester, gives bromnitrophenylmalonic ester,

$$C_6HBr(NO_2)_3CH(COOC_2H_5)_2,$$

by the replacement of 1 atom of bromine by the malonic ester radical, and of a second by hydrogen. No similar replacement of chlorine by hydrogen was observed in our work nor has one ever been observed so far as we can find. The tribromdinitrobenzol[4] and the trichlordinitrobenzol[5] show the same difference in their behavior toward sodic malonic ester as that which appears with the trinitro compounds.

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[1] Jackson and Koch: This JOURNAL, **21**, 510.

[2] *Ibid.*, **31**, 360 (1904).

[3] Jackson and Moore: *Ibid.*, **12**, 7 (1890).

[4] Jackson and Robinson: *Ibid.*, **11**, 93, 541 (1889).

[5] Jackson and Lamar: *Ibid.*, **18**, 664 (1896).

In our attempts to obtain a substitution of chlorine by hydrogen we treated the dichlortrinitrophenylacetic ester with sodic malonic ester, and obtained the replacement of a second atom of chlorine by the malonic ester radical, but our analysis of the substance was not sufficient to determine whether it was the chlortrinitrophenyleneaceticmalonic ester,

$$C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2,$$

or the chlortrinitrophenylenediacetic ester,

$$C_6Cl(NO_2)_3(CH_2COOC_2H_5)_2.$$

The latter would be the more probable, as the product was worked up by distillation with steam, but, as the analysis on the whole agrees better with the first formula, we have adopted that provisionally for this substance, which melts at 147° to 148°. Unfortunately the insufficiency of our analysis was discovered only after the departure of one of us from Cambridge prevented us from furnishing better analytical data. The bromtrinitrophenylmalonic ester[1] is also converted into trinitrophenylenedimalonic ester by the further action of malonic ester.

Further treatment with sodic malonic ester removed chlorine as sodic chloride from the chlortrinitrophenyleneaceticmalonic ester, but the organic product was so unmanageable that we can give no account of its nature.

The dichlortrinitrophenylacetic ester was converted by treatment with aniline into dianilinotrinitrophenylacetic ester,

$$C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5,$$

melting at 201°, which forms a compound with benzol,

$$C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5 2C_6H_6.$$

This result, taken in conjunction with those of Herman and one of us[2] on trianilinodinitrobenzol, and Carlton and one of us[3] on trianilinochlordinitrobenzol, indicates that the tendency to form addition-compounds is a marked one among nitroanilinobenzols. This subject will be studied more fully in this laboratory.

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[1] Jackson and Moore : This JOURNAL, **12**, 7 (1890).

[2] *Ibid.*, **16**, 35 (1894).

[3] *Ibid.*, **31**, 360 (1904).

When heated to 150° to 160° in a sealed tube with strong hydrochloric acid the dichlortrinitrophenylacetic ester was converted into a new 3,5-dichlor-2,4,6-trinitrotoluol, melting at 200° to 201°, by the saponification of the ester, followed by the removal of carbonic dioxide. Under the same conditions the chlortrinitrophenylenemalonicacetic ester gave a substance which, although not fully purified, was evidently the chlortrinitroxylol of Klages and Knoevenagel.[1]

The constitution of all the new compounds mentioned in this paper follows from the fact that they are prepared from the symmetrical 1,3,5-trichlor-2,4,6-trinitrobenzol.

EXPERIMENTAL PART.

Preparation of Trichlortrinitrobenzol.

The trichloraniline was prepared by the method of Victor Meyer and Sudborough,[2] that is, by passing chlorine through aniline dissolved in chloroform. The progress of the reaction was traced by filtering out a small quantity of the precipitate, washing it, and testing the aqueous washings with sodic hydrate ; the amount of the precipitate of aniline formed showed the extent of the chlorination. The trichloraniline was converted into trichlorbenzol by the action of alcohol sulphuric acid and sodic nitrite by the method of Lamar and one of us.[3] In that paper it is stated that the trichlorbenzol was converted into trichlordinitrobenzol by standing with fuming nitric acid of sp. gr. 1.505 in the cold. With commercial acid of sp. gr. 1.5 we obtained only the mononitro compound. Accordingly, we heated the trichlorbenzol on the steam-bath for several hours with a mixture of three parts of fuming nitric acid of sp. gr. 1.5 and one of fuming sulphuric acid of sp. gr. 1.89. The mixture, on standing over night, deposited nearly pure trichlordinitrobenzol. The small amount remaining in the acid mother-liquor was precipitated with water and purified by crystallization from alcohol.

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[1] Ber. d. chem. Ges., **28**, 2046 (1895).

[2] *Ibid.*, **27**, 3151 (1894) ; compare also Jackson and Lamar : This JOURNAL, **18**, 666 (1896).

[3] This JOURNAL, **18**, 667 (1896).

The trichlortrinitrobenzol was prepared by the method recently rediscovered by Mr. H. A. Carlton in this laboratory. We have found the following arrangement of the process gives the best yield. Sixteen grams of trichlordinitrobenzol were mixed with 400 cc. of fuming nitric acid of sp. gr. 1.50 and 160 cc. of fuming sulphuric acid of sp. gr. 1.89. The nitric acid was a nearly colorless commercial fuming acid. An acid strongly colored with nitrous fumes would probably fail to give the desired result judging from previous experience.[1] The sulphuric acid was prepared by mixing sulphuric trioxide with strong sulphuric acid. The mixture was boiled in a flask with the inner tube of a return-condenser ground into the neck (this condition is indispensable to success) for two days, the boiling being carried on violently the whole time. On standing over night a considerable quantity of the trichlortrinitrobenzol crystallized out in small, white needles, which were filtered out through glass wool. The filtrate was precipitated with water and the precipitate recrystallized from alcohol. When 16 grams of trichlordinitrobenzol were used, 7 to 8 grams of trichlortrinitrobenzol usually crystallized from the acid, and about 2 grams were obtained from the filtrate by precipitation.

In our last series of preparations the following yields were obtained from 100 grams of aniline:

Trichloraniline, an essentially quantitative yield.
Trichlorbenzol, 95 grams.
Trichlordinitrobenzol, 100 grams.
Trichlortrinitrobenzol, 48 grams.

The yield of trichloraniline is decidedly better than that obtained by Lamar and one of us,[2] but the yield of trichlorbenzol was only little over half of that formerly obtained.

Action of Sodic Ethylate on Trichlortrinitrobenzol.

One gram of trichlortrinitrobenzol was dissolved in 4 cc. of benzol and mixed with the sodic ethylate made from 0.6 gram of sodium and 15 cc. of absolute alcohol, so that there was a large excess of sodic ethylate. The solution turned bright scarlet on the addition of the first drops of the sodic ethylate, and there was a considerable evolution of heat. The mixture was allowed to stand an hour at ordinary temperatures, after which it was acidified with dilute sulphuric acid, which removed the red color, filtered from the precipitated salts, and evaporated on the steam-bath till the solvents had been driven off. The slightly oily, crystalline residue was recrystallized from alcohol until it showed a constant melting-point. As this lay at 119°, and the substance gave no test for chlorine, it was evidently the trinitrophloroglucine triethyl ether.[1] For greater certainty it was dried *in vacuo* and analyzed.

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[1] Jackson and Wing: This Journal, **9**, 348 (1887).

[2] *Ibid.*, **18**, 667 (1896).

0.2042 gram substance gave 23.1 cc. moist N_2 at 23° and 762 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.
N	12.17	12.78

The alcoholic mother-liquors from the trinitrophloroglucine triethyl ether contained a dark-green oil, from which we did not succeed in isolating any definite compound.

The precipitate obtained as one of the products of the reaction was in some cases filtered out before acidification. Upon washing with water most of it dissolved, and the solution after acidification with dilute sulphuric acid was concentrated and allowed to stand over night, when it deposited thick, yellowish-white needles, and, on further spontaneous evaporation, small, yellow, hexagonal prisms. The quantity was too small for complete purification, but both sorts of crystals melted from 160° to 165°. These observations show that the substance is the trinitrophloroglucine, $C_6(OH)_3(NO_2)_3.H_2O$, which melts with its water of crystallization at 160° to 161°, according to Warren and one of us,[2] at 158° according to Benedikt, but after being dried at 105° shows the melting-point 167°;[3] it also crystallizes in the two forms described.

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[1] Jackson and Warren: This JOURNAL, **15**, 611 (1893).

[2] *Ibid.*, **15**, 615 (1893).

[3] Ber. d. chem. Ges., **11**, 1376 (1878).

The behavior of trichlortrinitrobenzol with sodic ethylate therefore resembles that of tribromtrinitrobenzol with the same reagent so far as the replacement of halogen is concerned, but we observed no signs of the parallel reaction by which nitro groups are replaced in the tribromtrinitrobenzol.

Action of Sodic Malonic Ester on Trichlortrinitrobenzol.

Ten grams of trichlortrinitrobenzol were dissolved in 40 cc. of anhydrous benzol and mixed with the sodic malonic ester made by the action of 14 cc. of malonic ester and 2 grams of sodium previously treated with 40 cc. of absolute alcohol, that is, about 3 molecules of the malonic ester were used to each molecule of the trichlortrinitrobenzol. On the addition of the sodic malonic ester the mixture turned deep red, a precipitate was deposited, and there was a considerable evolution of heat. It was allowed to stand at ordinary temperatures in a corked flask for twenty-four hours, after which it was shaken with water in a separating-funnel, the oily layer acidified with dilute sulphuric acid, and washed with water. As the viscous residue obtained after the evaporation of the benzol showed no tendency to crystallize even after standing several days, the benzol solution was distilled with steam to remove the excess of malonic ester and perhaps other oily impurities. For this purpose the benzol solution was boiled with water in an evaporating-dish for fifteen to twenty minutes with constant stirring. On cooling, the organic substance solidified, and was found to be almost pure. Crystallization from alcohol raised it without difficulty to the constant melting-point, 130° to 131°, when it was dried *in vacuo* and analyzed. It is possible that a better solvent than alcohol could be found for this substance, if it were to be prepared in quantity, as alcohol brings about a decomposition of the compound when boiled for some time with it, shown by a darkening of the color and a lowering of the melting-point by about 2°. This prevents the easy isolation of additional pure material from the alcoholic mother-liquors.

I. 0.2455 gram substance gave, on combustion, 0.2960 gram CO_2 and 0.0573 gram H_2O.

II. 0.2222 gram substance gave 0.2632 gram CO_2 and 0.0432 gram H_2O.

III. 0.1792 gram substance gave, by the Carius method, 0.1391 gram AgCl.

IV. 0.1816 gram substance gave 0.1415 gram AgCl.

V. 0.2126 gram substance gave 0.1614 gram AgCl.

VI. 0.1574 gram substance gave 0.1237 gram AgCl.

	Calculated for $C_6Cl_2(NO_2)_3CH_2COOC_2H_5$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	32.60	32.87	32.30	....	....	....	....
H	1.90	2.61	2.18	....	....	....	....
Cl	19.30	....	....	19.19	19.26	18.77	19.43

The substance is therefore the dichlortrinitrophenylacetic ester instead of the expected malonic ester. We were unable to determine whether the acetic ester was the direct product of the reaction or formed from the substituted malonic ester during the boiling with water, as all our attempts failed to isolate the product of the reaction without boiling it with water. The results of the work of Carlton and one of us[1] with trichlordinitrophenylmalonic ester indicate that the acetic ester is formed during distillation with steam, but they are not conclusive.

Properties of Dichlortrinitrophenylacetic Ester, $C_6Cl_2(NO_2)_3CH_2COOC_2H_5$.—It crystallizes in long, slender, white prisms, usually terminated by a single plane at an oblique angle, which are arranged in radiated groups. It melts at 130° to 131°, and is freely soluble in benzol, chloroform, or acetone; soluble in cold ethyl or methyl alcohol, ether, carbonic disulphide, or glacial acetic acid, more soluble in each of these solvents when hot; slightly soluble in ligroin; insoluble in water. The three strong acids have no action on it in the cold, and hydrochloric acid does not attack it when hot (except by long-continued heating). Hot, strong nitric acid gives a yellow solution with it; hot sulphuric acid a brown solution. A hot, aqueous solution of sodic hydrate gives a red solution with it, which undoubtedly contains its sodium salt.

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[1] This JOURNAL, **31**, 360 (1904).

Dianilinotrinitrophenylacetic Ester, $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5$.—One gram of the dichlortrinitrophenylacetic ester was treated with an excess of aniline. The first drops of the aniline gave a bright red color at once, but on acidification and washing only a very slight precipitate could be obtained from the wash-waters with argentic nitrate. It seems possible, therefore, that this red color is due to the aniline salt of the phenylacetic ester. The mixture of aniline and the substance was accordingly heated on the steam-bath for two hours, at the end of which time it had solidified. After washing out the excess of aniline with dilute hydrochloric acid and water it was purified by crystallization from benzol, when it was found that it combined with 2 molecules of benzol to form yellow crystals, but if the crystallization took place under ordinary conditions, in addition to these yellow crystals small red needles, free from benzol, were deposited. In order to obtain only the compound containing benzol, we proceeded as follows: Some of the substance was dissolved in benzol with the aid of heat—it dissolves with difficulty in the cold—and the solution cooled by immersing the beaker in snow. The benzol was then evaporated off by passing a current of air over its surface, and in this way the yellow crystals, without a trace of the red, were obtained. They were dried on a porous plate, washed with a little cold benzol, and dried for analysis by exposure to the air in a cold place.

1.4451 grams substance lost, at 100°, 0.3829 gram.

	Calculated for $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5.2C_6H_6$.	Found.
C_6H_6	24.53	26.50

This result is much further from the theoretical number than we could wish, but it lies still further from the percentage calculated for a compound with 3 molecules of benzol (32.77), and, as it represents an additional loss of only about 10 milligrams, an amount of benzol or moisture which might easily have been present considering the imperfect method of drying necessary on account of its instability, we think there can be no doubt that the formula given is correct. That the substance lost was benzol was proved by heating a sample in a test-tube, when a vapor was obtained recognized as benzol by its smell and method of burning.

Properties of the Benzol Addition-Compound of Dianilinotrinitrophenylacetic Ester.—It forms beautiful, golden-yellow crystals, which lose the benzol between 20° and 30° in a few hours, more rapidly at 100°. Owing to the ease with which the benzol is given off, this substance melts at the same temperature as the dianilinotrinitrophenylacetic ester, 201°.

The mixture of yellow and red crystals obtained in making dianilinotrinitrophenylacetic ester was crystallized from benzol until it showed the constant melting-point 201°, when it was dried at 100° and analyzed with the following result:

0.2527 gram substance gave 0.5146 gram CO_2 and 0.1067 gram H_2O.

	Calculated for $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5$.	Found.
C	54.89	55.54
H	3.95	4.73

The result obtained is perhaps as near as could be expected, since the body decomposes explosively a few degrees above its melting-point. To meet this difficulty the substance was thoroughly mixed with fine cupric oxide in a copper boat about 15 cm. long, and the heat was applied with great caution. The analysis leaves no doubt as to the formula of the compound.

Properties of Dianilinotrinitrophenylacetic Ester, $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5$.—It crystallizes from benzol at ordinary temperatures in long, slender, red prisms, terminated by a single plane at an oblique angle, but these prisms are usually mixed with yellow crystals of the benzol compound. It melts at 201°, and is freely soluble in acetone; soluble in chloroform when cold, freely soluble when hot; slightly soluble in cold benzol, freely in hot; slightly soluble in cold ether, carbonic disulphide, or glacial acetic acid, soluble in each of these solvents when hot; essentially insoluble in cold ligroin or methyl alcohol, soluble when hot; essentially insoluble in ethyl alcohol, slightly soluble in it when hot; insoluble in water. Strong hydrochloric acid has no action on it; strong nitric acid has no action in the cold, but gives a yellow solution if hot; strong sulphuric acid gives a wine-colored solution in the cold, and chars it when hot. Sodic hydrate gives a yellow solution when hot.

Saponification of Dichlortrinitrophenylacetic Ester.

As our preliminary experiments on the action of sulphuric acid of sp. gr. 1.44 led to unsatisfactory results, we used strong hydrochloric acid as the saponifying agent. Five-tenths gram of the dichlortrinitrophenylacetic ester were heated with 4 cc. of strong hydrochloric acid in a sealed tube to 150° to 160° over night. The yellowish-white crystalline product was purified by crystallization from a mixture of three parts of alcohol with one of water, until it showed the constant melting-point 200° to 201°, when it was dried at 100°, and analyzed with the following result:

I. 0.1442 gram substance gave, by the Carius method, 0.1382 gram AgCl.

II. 0.2060 gram substance gave 0.1986 gram AgCl.

	Calculated for $C_6Cl_2(NO_2)_3CH_3$.	Found. I.	II.
Cl	23.99	23.69	23.84

The substance is therefore the dichlortrinitrotoluol,

$$Cl_2 3,5 \cdot (NO_2)_3 2,4,6,$$

and we cannot find that it has been described as yet. Two grams of the dichlortrinitrophenylacetic ester gave 1.4 grams of the dichlortrinitrotoluol, that is, 87 per cent of the theoretical yield.

Properties of the 3,5-Dichlor-2,4,6-trinitrotoluol, $C_6Cl_2(NO_2)_3CH_3$.—It crystallizes from dilute alcohol in white, long, slender, flat prisms, terminated by one plane at a sharp angle; less commonly in little crystals looking like elongated rhombohedra, probably the same form as the first but not flattened. It melts at 200° to 201°, and is freely soluble in benzol or acetone; soluble in cold chloroform, freely soluble in it when hot; slightly soluble in cold alcohol, freely in hot;

slightly soluble in methyl alcohol, ether, ligroin, carbonic disulphide, or glacial acetic acid when cold, soluble in each of these solvents when hot; insoluble in water. The best solvent for it is a mixture of three parts of alcohol with one of water. It is not affected by the three strong acids, or sodic hydrate even when hot.

Chlortrinitrophenyleneaceticmalonic Ester, $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$.—Five grams of dichlortrinitrophenylacetic ester were dissolved in as little benzol as possible and mixed with the sodic malonic ester made from 5.2 cc. of malonic ester and 0.75 gram of sodium previously treated with 30 cc. of absolute alcohol, that is, 2 molecules of sodic malonic ester to 1 of the phenylacetic ester. On the addition of the sodic malonic ester the solution turned dark-claret, but there was no perceptible evolution of heat. The mixture was allowed to stand over night in a corked flask at ordinary temperatures when it was found that it had taken on a scarlet color. It was worked up by precipitation with water, acidifying the benzol solution with dilute sulphuric acid, washing again, and boiling for fifteen or twenty minutes with water in an evaporating dish with constant stirring. The product solidified on cooling, and was purified by crystallization from alcohol until it showed the constant melting-point 147° to 148°, when it was dried *in vacuo* and analyzed with the following results:

0.2569 gram substance gave, on combustion, 0.3867 gram CO_2 and 0.0809 gram H_2O.

	Found.
C	41.06
H	3.50

This analysis is not sufficient to establish the composition of the substance with certainty, and, as its insufficiency was not recognized before the departure of one of us from Cambridge, we are unable to add the necessary analytical data, but, although the nature of the body cannot be stated with certainty, our results lead to a very probable formula for it which we have adopted provisionally. The two probable formulas for it are,

I. $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$,

formed by the replacement of a second atom of chlorine by the malonic ester radical, and,

II. $C_6Cl(NO_2)_3(CH_2COOC_2H_5)_2$,

formed from I. by saponification, followed by the removal of carbonic dioxide. The following table gives a comparison of the percentages of carbon and hydrogen in Formulas I. and II. with those found in our analysis :

	I.	Found.	II.
C	41.54	41.06	40.05
H	3.67	3.50	3.34

Our analytical results agree better with Formula I. than with II., but the percentage of water is actually smaller than that contained in Formula I., where it would be expected to be decidedly higher in a substance like this containing chlorine. On the other hand, the percentage of carbon found is a whole per cent above that contained in Formula II., and, if this were due to chlorine, which had escaped absorption, the hydrogen found must have come more than 0.16 per cent too high. It seems to us, therefore, that the more probable formula is I., and that the body may be called provisionally the chlortrinitrophenyleneaceticmalonic ester.

The yield was 2.4 grams of the new substance from 5 grams of dichlortrinitrophenylacetic ester, that is, 35 per cent of the theoretical yield.

Properties of the Chlortrinitrophenyleneaceticmalonic Ester, $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$.—It crystallizes from alcohol in white, much-branched needles, at first arranged in round, radiating groups, which develop later into forms like birch rods. It melts at 147° to 148°, and is freely soluble in benzol, chloroform, or acetone ; soluble in cold ether or carbonic disulphide, freely soluble in them when hot ; soluble in cold ligroin, more soluble in hot, but not freely so ; slightly soluble in ethyl or methyl alcohol or glacial acetic acid when cold, soluble when hot ; insoluble in water. The best solvent for it is alcohol. The three strong acids have no action on it in the cold, and hot hydrochloric acid does not affect it; hot nitric acid forms a red solution with it; hot sulphuric acid chars it. A hot aqueous solution of sodic hydrate gives a deep red solution with it—undoubtedly the sodium salt.

Attempts to saponify this substance in the usual way with sulphuric acid led to unsatisfactory results. With strong hydrochloric acid, at 160° to 170°, in a sealed tube, a well-crystallized body was obtained, but we did not have time to prepare enough of it for complete purification. As it melted in an impure state between 215° and 220°, there can be little doubt that it was the expected 5-chlor-2,4,6-trinitroxylol, which melts, according to Klages and Knoevenagel,[1] at 218°.

Upon treating the so-called chlortrinitrophenyleneaceticmalonic ester with sodic malonic ester, sodic chloride was formed, but no definite organic compound could be isolated from the sticky black product.

REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS. By DR. C. REMIGIUS FRESENIUS, Director of the Chemical Laboratory at Wiesbaden. Authorized translation of the Sixth German Edition, by ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1904. 8vo. 2 Vols. pp. xxxiv + 2035. Cloth, $12.50.

There is surely no occasion here to make any special reference to the many and peculiar excellencies of the last German edition of this work, hence the reviewer will mainly confine his remarks to points in which this translation appears to differ from the sixth German edition.

In accordance with the views of the author of this important treatise on Quantitative Analysis, the translator presents a judicious transformation of the out-of-date terminology to forms according with more modern views, still retaining the binary expression of the composition of salts; what is otherwise so well done is marred by the statement of the composition of potassium nitrate as KO and NO_2, and similarly of sodium nitrate, a view distinctly not harmonious with the rest of the book.

This translation exhibits less of German idiom than does the recent English edition of this work, and it has generally omitted nothing of the original text. Leading the type gives a decided improvement in the appearance of the pages over that of the English edition, but this change alone adds over a third to the bulk and the cost of the book. Surely it would have improved the work to have left out the detail of such preparations as that of potassium permanganate and of hydrofluoric acid, now that these reagents are so readily obtainable in sufficient purity, the latter in ceresine bottles.

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[1] Ber. d. chem. Ges., **28**, 2046 (1895).

The numberings of the paragraphs are unchanged, and, generally, these are thrown into an improved form, all additions being brought in under sub-heads. Many valuable additions to the methods of determination have been introduced, among which are: Penfield's estimation of fluorine, Rose's estimation of carbon dioxide by volume, the precipitation of zinc sulphide in a hot solution, the precipitation of manganese by bromine and ammonia, the decomposition of silicates by sulphuric and hydrofluoric acids, Schulze's estimation of nitric acid, and a full and clear description of basic acetate precipitation. A satisfactory description of Dr. J. Lawrence Smith's method of estimating alkalies in silicates is given, but, unfortunately, this latter operation is twice indexed as a method of determining silica.

Dr. Gibbs' method of precipitating copper oxide by sodium carbonate is given, but there is no mention of the addition of sodium hydroxide, which addition affords a very satisfactory modification of this otherwise troublesome process (see Proc. Am. Chem. Soc., II., No. 4).

The precipitation of alumina by ammonia is properly improved by shortening the time of heating, but the use of paper pulp to promote the washing of this precipitate is not mentioned.

Some excellent methods of procedure now in use by analysts, which one might have expected to find here, have been omitted, especially the ignition of some sulphides under hydrogen sulphide, which is to be preferred to hydrogen, in determining cuprous sulphide, lead sulphide, cobalt sulphide, zinc sulphide, etc. (Ztschr. anal. Chem., **19**, 172).

Quite a number of important modifications of older methods have been given in the appendix of Vol. II., which one would expect to find in Vol. I. or at least referred to there, such as the proper method of precipitating ammonium magnesium phosphate, the washing of "yellow precipitate" with diminishing amounts of ammonium nitrate in lieu of molybdate solution, Dr. Gooch's use of amyl alcohol to separate lithia, Weller's method of detecting and estimating titanic oxide by hydrogen dioxide.

In Volume II. we find also a number of new processes given in detail, including the following: The use of Johnson and Jenkins' azotometer, the methods of Clennell and of Handy for zinc, Gautier's separation of arsenic according to Johnson and Chittenden, electrolytic separation of lead by Hollard and of copper by Gooch, Oma Carr's estimation of tannic acid, G. Tate's method for silica in ferro-chrome, and a volumetric estimation of manganese by F. W. Daw. Dr. Gibbs' use of a comparison tube in measuring gases is described, also an improved form of purifier for oxygen is mentioned, which suggests the omission of the very efficient and compact apparatus devised for this purpose by F. G. Benedict (see this JOURNAL, **23**, 332). There is also given an improved method of burning carbon from iron in oxygen, but no notice has been taken of the excellent suggestion of T. W. Hogg of the use of a mixture of ferric and cupric chlorides for the separation of carbon from iron or steel (see Chem. News, **58**, 199).

When a full table of the strength of acetic acid by Oudemans was given on page 291, there does not appear any reason for the translator adding, on page 318, a similar table by Mohr, which has less range and is not definite as to temperature.

In the examples for practice, a peculiarly full and lucid description is given of the exact process in the determination of chlorine in sodium chloride, which will prove of much value as a lesson in accurate manipulation to any beginner in analysis.

In Appendix I. we find in full the official methods of analysis of the agricultural chemists, being a reprint of Chemistry Bulletin No. 46 of the U. S. Department of Agriculture, so presenting in a convenient and permanent form data which every analytical chemist should have at hand.

In Appendix II. we have a reprint of the admirable paper on mineral analysis by Dr. W. F. Hillebrand, as published in Bulletin No. 176 of the U. S. Geological Survey. This includes quite a number of the more recent improved methods, to which, as before noted, it would have been well to have referred in the schemes given in Volume I.

The very full index is presented in a clear and attractive form and the work of the printer is well done throughout the book. F. P. D.

THE PHASE RULE AND ITS APPLICATIONS. By ALEX. FINDLAY, M.A., PH.D., D.SC., Lecturer and Demonstrator in Chemistry, University of Birmingham; with an INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY, by SIR WILLIAM RAMSAY, K.C.B., F.R.S. New York: Longmans, Green & Co. 1904. pp. 313.

Only words of praise can be spoken for this admirable little book. We have at last a treatise on the Phase Rule in English, which is clear, concise, and intelligible to any earnest student of physical chemistry. This book compares favorably with the more elaborate treatise in German on the same subject by Roozeboom.

The most important chapters are on Typical Systems of One Component; Systems of Two Components—Dissociation; Solutions of Gases, Liquids, Solids; Systems of Three Components; Systems of Four Components.

The work is prefaced by an introduction to Physical Chemistry by Sir William Ramsay, which is really a brief, historical sketch of physical chemistry from the earliest time. The work can be heartily recommended to every one who wishes to become familiar with the development of this important generalization, which we owe originally to our distinguished countryman, Willard Gibbs, but which has been developed in the hands of modern physical chemists. H. C. J.

A LABORATORY MANUAL OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY FOR STUDENTS IN MEDICINE. By DR. E. SALKOWSKI, Professor in the University and Director of the Chemical Laboratory of the Pathological Institute, Berlin. Authorized translation from the second revised and enlarged German edition. By W. R. ORNDORFF, A.B., PH.D., Professor of Organic and Physiological Chemistry in Cornell University. First edition. New York: John Wiley & Sons. pp. 263.

The translation of Salkowski's Practicum will be welcomed by all physiological chemists who have to do with the teaching of the subject on account of the number of medical students who cannot read German satisfactorily. Ever since this work was written it has been the model of laboratory manuals in physiological chemistry. In some respects the work has not been kept up to date, however. On page 49 the decomposition of hydrogen peroxide by blood is spoken of as the "so-called catalytic action of the blood pigment." It was shown by Bergengruen, in 1888, that pure hemoglobin does not decompose hydrogen peroxide, and that the action of blood on hydrogen peroxide is due to the stroma of the red blood corpuscles. Again, the work of Schiff on the biuret reaction might have been mentioned, and also the work of Hopkins and Cole on tryptophan.

Again, Salkowski's old method for the separation of the xanthine bases is given instead of the far more satisfactory method of Krüger and Salomon, which is now almost exclusively used.

The translation is clear and satisfactory and it deserves to be largely used. A. S. L.

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AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN SULPHAMIDO DERIVATIVES OF FURFURANE.[1]

BY H. B. HILL AND J. P. SYLVESTER.

The object of this research was to determine whether sulphinides could be formed in the furfurane series. Of the two methods for preparing these bodies in the aromatic series, that[2] by oxidation of orthomethylsulphamides was inadmissible here, because of the instability of the furfurane ring toward oxidizing agents. Accordingly, all the work was done by the second method,[3] consisting in treating with ammonia the chloride of an ortho-β-sulphocarboxyl acid. We have studied in this way three different pyromucic acids, β-sulpho-δ-methylpyromucic acid,[4] β-sulpho-δ-chlorpyromucic acid,[5] and β-sulpho-δ-brompyromucic acid.[1] Each of the first two of these acids was treated with phosphoric pentachloride in quantity sufficient to form the chloride, $RSO_2Cl.COCl$, while with the third acid it was necessary to use phosphoric pentabromide as the chloride brought about a partial replacement of the bromine on the furfurane ring by chlorine. The chloride (or bromide) was then treated with ammonic hydrate, but instead of obtaining the sulphinide, $RCONHSO_2$, as happens in the benzol group, the result was in every case a diamide. β-Sulphamido-δ-methylpyromucamide,

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[1] The experimental work of this research was carried on under Professor Hill's supervision several years ago, but it has been prepared for publication since his untimely death. The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by J. P. Sylvester. C. L. J.

[2] Remsen and Fahlberg: This JOURNAL, **1**, 426.

[3] Remsen and Fahlberg: *Ibid.*, **1**, 437.

[4] Hill and Jennings: *Ibid.*, **15**, 174 (1893).

[5] Hill and Hendrixson: *Ibid.*, **15**, 151 (1893).

$$C_4HOCH_3.SO_2NH_2.CONH_2,$$

melts at 196° to 197°. β-Sulphamido-δ-chlorpyromucamide,

$$C_4HOCl.SO_2NH_2.CONH_2,$$

melts at 212°. β-Sulphamido-δ-brompyromucamide,

$$C_4HOBr.SO_2NH_2.CONH_2,$$

melts at 219° to 220°.

With a solution of baric hydrate these diamides give off ammonia even in the cold, but instead of the sulphinide hoped for, a β-sulphamidopyromucic acid is formed, and the acids thus obtained did not pass easily into the sulphinides like the corresponding orthosulphamidobenzoic acids. On the contrary, they remained essentially unaltered even when heated alone, or with hydrochloric acid, or oxalic acid. Sulphuric acid had no action in the cold, but charred the substance when hot. The result of our experiments, therefore, is that sulphinides of the furfurane group are not formed under conditions which produce them in the benzol group. Whether they can be made under any conditions must be left to future experiments to decide.

The β-sulphamido-δ-methylpyromucic acid,

$$C_4HOCH_3.SO_2NH_2.COOH,$$

melts at 217° to 218°. The β-sulphamido-δ-chlorpyromucic acid,

$$C_4HOCl.SO_2NH_2.COOH,$$

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[1] Hill and Sanger: Proc. Am. Acad. Sci., **21**, 138; Ann. Chem. (Liebig), **232**, 42.

melts at 194° to 195°. The β-sulphamido-δ-brompyromucic acid,

$$C_4HOBr.SO_2NH_2.COOH,$$

melts at 190° to 191°. Several salts of each of these acids are described. In making the methyl acid the preparation runs essentially without secondary products, but with the chlor- and bromacids a few per cent of the diamide are decomposed with destruction of the furfurane ring.

The action of bromine and water on these sulphamidopyromucic acids gave the following substituted furfuranes:

$C_4HOCH_3Br.SO_2NH_2$, melting-point 123°;
$C_4HOClBr.SO_2NH_2$, melting-point 134° to 135°;
$C_4HOBr_2.SO_2NH_2$, melting-point 153° to 154°.

Further treatment of these substances with bromine and water gave from the methyl compound sulphoacetacrylic acid,

$$CH_3COCHC.COOH.SO_3H,$$

from the two halogen compounds sulphofumaric acid,

$$C_2H.SO_3H(COOH)_2.$$

EXPERIMENTAL PART.

Derivatives of δ-Methylpyromucic Acid.

The pure methylfurfurol needed for the preparation of methylpyromucic acid was obtained by fractional distillation of a large number of impure samples of the oil boiling higher than furfurol obtained from the distillation of wood. The chief impurities were furfurol, and, in much smaller amount, the high-boiling constituents of the crude furfurol oil.

In the preparation of the acid through the oxidation of methylfurfurol by means of argentic oxide, the method described by Sawyer[1] and one of us was followed essentially. It was found, however, that it was not necessary to wash the argentic oxide used in the reaction. One hundred and ten grams of argentic nitrate, giving 75 grams of argentic oxide, were freshly precipitated by means of sodic hydrate in a two-liter flask, the precipitate allowed to settle, and the solution of sodic nitrate decanted. This decantation was found necessary to prevent the serious bumping which occurred if all the sodic nitrate was left in solution and boiled in the oxidation-flask. To the argentic oxide were then added about 15 grams of sodic hydrate dissolved in 1 liter of water. It was found advisable thus to increase the amount of alkali, as if 11 grams, the amount theoretically necessary to form the sodium salt with all the acid produced, were used, some silver was found in solution after filtration. Thirty grams of methyl furfurol were now introduced, and the contents of the flask boiled for thirty minutes with a return-condenser. The sodium salt was then filtered and the methylpyromucic acid separated by means of hydrochloric acid. The yield varied from 88 to 94 per cent. As the acid was somewhat dark in color, it seemed advisable to purify it by the method suggested by Jennings and one of us[1] before converting it into the sulphonic acid. From all samples, therefore, the calcium salt was prepared, a dilute solution of which was boiled for some time with bone-black and then acidified. After this treatment the acid was almost pure white and melted at 107° to 108°, indicating a sufficient degree of purity for the purpose at hand.

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[1] This Journal, **20**, 171.

Jennings[2] and one of us have described and analyzed the barium salt of sulphomethylpyromucic acid. This method of preparing the salt was followed. Methylpyromucic acid was slowly added to three times its weight of fuming sulphuric acid while the mixture was well stirred and cooled. The viscous solution was allowed to stand twenty-four hours, then largely diluted with water and neutralized with baric carbonate. The aqueous solution of the barium salt of the sulphonic acid was filtered from the baric sulphate and excess of carbonate. Since the potassium salt was desired as a starting point for further work, the barium was precipitated with potassic carbonate and the filtered solution evaporated to small volume, when, upon cooling, the potassium salt crystallized out. The salt thus obtained was almost white, but was purified for the following work by a single recrystallization from hot water. The amount of potassium salt thus prepared from methylpyromucic acid was from 70 to 80 per cent of the theoretical yield. As this salt has never been described, a small amount of it was purified for analysis by three further recrystallizations from water.

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[1] This JOURNAL, **15**, 167 (1893).

[2] *Ibid.*, **15**, 175 (1893).

Potassic Sulphomethylpyromucate, $K_2C_6H_4SO_6.2H_2O$.—The salt is very readily soluble even in cold water, and its solubility is somewhat increased by heat. It crystallizes in prisms, usually long and slender, the opposite sides of which are parallel. The ends are not quite rectangular. The air-dried salt contains 2 molecules of water and begins to effloresce slowly over sulphuric acid. Heated to 130°, the salt becomes anhydrous very quickly. The determination of the potassium was not a very easy matter. It was found difficult to decompose the salt by means of nitric acid, sulphuric acid, or a mixture of the two without loss by spattering. Finally, however, the analysis was carried through successfully by oxidizing the salt with a comparatively large amount of nitric acid, 6 or 7 cc., and applying heat very slowly and gradually. The nitric acid was followed by sulphuric acid and the potassium weighed as sulphate, as usual.

I. 1.6032 grams air-dried salt lost, at 130°, 0.1814 gram H_2O.

II. 1.3739 grams air-dried salt lost, at 130°, 0.1555 gram H_2O.

	Calculated for $K_2C_6H_4SO_6.2H_2O$.	Found. I.	II.
H_2O	11.30	11.31	11.31

I. 0.5951 gram salt, dried at 130°, gave 0.3661 gram K_2SO_4.

II. 0.6201 gram salt, dried at 130°, gave 0.3800 gram K_2SO_4.

	Calculated for $K_2C_6H_4SO_6$.	Found. I.	II.
K	27.72	27.62	27.51

β-Sulphamido-δ-methylpyromucamide.

Ten grams of anhydrous potassic sulphomethylpyromucate were powdered and placed in a small boiling-flask. To this was added finely divided phosphoric pentachloride in the proportion of 1 molecule of each, and the two substances were well mixed by shaking. The reaction began at once with a slow evolution of heat and partial liquefaction of the contents of the flask. The flask was then placed in an oil-bath and heat gradually applied till the temperature of the bath reached 160°, at which point the temperature was kept from two to three hours. At most, only a few drops of phosphoric oxychloride distilled off. On one occasion, instead of heating at 160°, the bath remained at 120° for half an hour, and the flask stood in a desiccator over night. Under these conditions, also, the reaction was complete; and the yield and purity of the final amido product were the same as in cases where the phosphoric pentachloride was allowed to react at the higher temperature. The treatment of the double acid chloride formed was the same in all cases. The flask was cooled and the viscous contents shaken out into a beaker containing about 100 cc. of cold water. The oily chloride, together with the potassic phosphate and chloride, were well stirred until the potassium salts had dissolved. The emulsion thus formed was poured into a separating-funnel, allowed to settle, and further washed by shaking several times with cold water, which could be done with impunity as the double chloride did not seem particularly reactive with water at 10° to 15°.

The washed chloride was slowly poured, drop by drop, into the strongest ammonic hydrate, which was vigorously stirred and cooled to a temperature of about 10° during the progress of the reaction. The addition of the chloride usually required about an hour; if too much were added at one time, the heat developed was sufficient to cause an ebullition on the bottom of the beaker, which was found to indicate that the reaction was going too fast, and that if not retarded by cooling and stirring, a dark product and low yield would result. If the temperature were in the neighborhood of 0° the reaction proceeded very slowly. After all the chloride had been added, the beaker containing the ammoniacal solution was allowed to stand at the temperature of the room for twenty-four hours. By the end of this time a large part of the ammonia had evaporated, and more or less of the double amide had crystallized out. The solution was heated on the steam-bath until all the ammonia was gone. Then hot water was added, if necessary, in sufficient quantity to dissolve all the amide, the solution cooled, and the crystals separated from the mother-liquor by filtration. The weight of sulphamidomethylpyromucamide obtained varied from 80 to 85 per cent of the theoretical yield. It melted only 1° or so below the melting-point of the pure substance, yet it was invariably somewhat dark in color. This color we failed to remove completely by repeated crystallizations from water, but boiling a solution of the original product with bone-black yielded a substance which was perfectly white. A small amount of the pure white amide was recrystallized from water several times to purify it for analysis. After the first recrystallization the melting-point was not raised, nor was it changed if alcohol were used as a solvent. The substance was evidently pure and was therefore analyzed with the following results:

I. 0.1998 gram substance gave, on combustion, 0.2569 gram CO_2 and 0.0743 gram H_2O.

II. 0.1915 gram substance gave 0.2457 gram CO_2 and 0.0694 gram H_2O.

III. 0.2114 gram substance gave 0.2431 gram $BaSO_4$.

IV. 0.2131 gram substance gave 0.2453 gram $BaSO_4$.

	Calculated for $C_6H_8N_2SO_4$.	Found. I.	II.	III.	IV.
C	35.27	35.06	35.00	....	....
H	3.95	4.16	4.05	....	....
S	15.70	....	....	15.79	15.82

β-Sulphamido-δ-methylpyromucamide.—This substance melts at 196° to 197°. It is very readily soluble in hot water, sparingly in cold. Its aqueous solution is neutral to litmus. Alcohol dissolves it easily, but the solvent power does not change with heat so much as is the case with water. It is insoluble in ether, carbon disulphide, or benzol, and very sparingly soluble in chloroform. From a hot aqueous solution it crystallizes in obliquely terminated prisms which are usually clustered and long and slender. Sometimes, however, they form single and somewhat broader prisms.

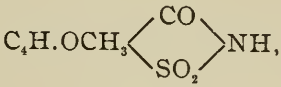
If the phosphoric pentachloride acts normally, a substance like potassic sulphomethylpyromucate would theoretically require 2 molecules of pentachloride for each molecule of the salt. It has been found, however, as stated above, that 1 molecule of phosphoric pentachloride forms a chloride which, after treatment with ammonia, yields 80 to 85 per cent of the theoretical amount of amide. Taking into account the mechanical losses due to washing and separating the oily chloride, and the amount of amide in the mother-liquor, this yield shows that the formation of the double chloride from the potassium salt must have been nearly quantitative, which can be explained by supposing that the phosphoric oxychloride took part in the reaction.

As it seemed of interest to see what effect an additional molecule of phosphoric pentachloride would have, twice the usual amount was tried. In this case a considerable quantity of phosphoric oxychloride distilled over, the thermometer in its vapor reading 107°, while the bath was 160°. In the treatment of the oil with water more heat was developed, and the oil and the amide were darker than usual, but the percentage yield was exactly the same as in the previous preparations. Obviously, then, there was nothing to be gained by using 2 molecules of phosphoric pentachloride.

The acid chloride, which is the product of the phosphoric pentachloride reaction, is a heavy, viscous oil, which did not solidify at 0°. It was not purified except by washing with water, as described above, and was not analyzed. In all cases it was converted immediately into the amide, which has the following formula :

$$C_4HOCH_3.SO_2NH_2.CONH_2.$$

This product is of interest because it brings out a difference in behavior between corresponding compounds of the benzol and furfurane series. Under similar treatment sulphobenzoic acid yields benzoic sulphinide, consequently the substance expected was



$$C_4H.OCH_3\langle{}^{CO}_{SO_2}\rangle NH,$$

which differs from the product obtained by 1 molecule of ammonia

β-Sulphamido-δ-methylpyromucic Acid.

When treated with solutions of alkalies, the double amide gave off ammonia even in the cold, and this result was obtained also with baric hydrate. To determine whether all the nitrogen was removed, or if not, what was the acid from which the salt was formed, the following experiment was tried: Four and three-tenths grams of the double amide were placed in a flask and boiled for four hours with baric hydrate, dissolved in 200 cc. of water in the proportion of about 2 molecules of hydrate for each of the amide; at the end of this time no more ammonia was evolved. To collect the ammonia given off, the condenser was connected by a delivery-tube with another flask containing water, and the amount of the ammonia given off was approximately determined at the end of the reaction by titrating the contents of this second flask with a standard hydrochloric acid solution. In this way the presence of 0.366 gram of ammonia was shown, while the amount calculated for 1 molecule was 0.358 gram. The excess of barium was precipitated with carbonic dioxide, and the filtered solution evaporated to a rather small volume. On cooling, 4.6 grams of a crystalline substance were deposited. Qualitative tests showed this to be the barium salt of an acid containing nitrogen and sulphur. The barium was precipitated by sulphuric acid, and the filtrate, upon evaporation, yielded crystals which caused effervescence with carbonates, gave a solution strongly acid to litmus, and melted some 20° higher than the original amide. They, too, contained nitrogen and sulphur and, therefore, were either the sulphamido acid or its anhydride, the sulphinide. Accordingly, more of this acid was prepared from the amide in a similar manner except that the boiling with baric hydrate solution took place in an open flask, which shortened somewhat the time necessary to expel all the ammonia. The yield was satisfactory, as 65 per cent of the theoretical amount of this acid was usually obtained starting from potassic sulphomethylpyromucate. The barium salt was often somewhat colored, and was purified before making the acid, sometimes by the use of boneblack, which was moderately effective, and sometimes by simple recrystallization. The sample of acid used for analysis was made from a barium salt recrystallized four times. The acid itself was then submitted to several crystallizations from water. Further recrystallization of a small amount failed to alter the melting-point. The substance was therefore dried *in vacuo* and analyzed.

I. 0.2205 gram substance gave, on combustion, 0.2823 gram CO_2 and 0.0748 gram H_2O.

II. 0.2198 gram substance gave 0.2818 gram CO_2 and 0.0738 gram H_2O.

	Calculated for $C_6H_7NSO_5$. I.	$C_6H_5NSO_4$. II.	Found. I.	II.
C	35.10	38.48	34.92	34.96
H	3.44	2.69	3.79	3.76

These analyses made it perfectly evident that the body in question was sulphamidomethylpyromucic acid, I., and not its anhydride, II.

β-Sulphamido-δ-methylpyromucic Acid. — This substance melts at 217° to 218°, and is readily soluble even in cold water. From a hot aqueous solution it crystallizes generally in clusters of long, slender, rectangular prisms. Occasionally these prisms are broadened and shortened, until at times they appear almost cubical. The acid is distinctly more soluble in cold alcohol than in water. It is insoluble in benzol, carbonic disulphide, or chloroform, while in ether it dissolves with difficulty.

In order to learn whether there was any tendency for this acid to form the anhydride, it was submitted to several different treatments favorable to dehydration. 2.5013 grams air-dried acid lost nothing in a desiccator over sulphuric acid for five days. 2.0442 grams acid, dried over sulphuric acid, lost only 0.0007 gram in four hours at 100°, and only 0.0012 gram more when heated four hours at 160°. Of course, this total loss of 0.09 per cent is insignificant.

0.1123 gram was placed in a small test-tube and heated in an oil-bath at a temperature a few degrees above the melting-point of the substance for half an hour. The test-tube was allowed to cool in a desiccator and weighed. The acid lost 0.0097 gram, or 8.64 per cent. The loss calculated for 1 molecule of water is 8.78 per cent. This seemed encouraging, but further study led to the conclusion that this agreement was merely accidental, and that the loss in weight was due to decomposition, not to the formation of an anhydride, for the substance had blackened very considerably; benzol and chloroform would dissolve nothing, while after treatment with water and filtering from the charred residue, which alone was insoluble, the original acid was deposited in its characteristic crystalline form.

A small amount of the substance dissolved without blackening in about 1 cc. of strong sulphuric acid. At the end of an hour it was poured into twice its volume of water. As nothing separated, the solution was extracted with ether, but the ether extract yielded only a small amount of crystals resembling the original acid, and it was shown by another experiment that the acid in aqueous solution could be extracted with ether to some extent.

In another trial the acid, dissolved in sulphuric acid, was heated to 100° when a lively effervescence of sulphurous dioxide set in, accompanied by intense blackening.

Equally unsuccessful was an attempt to dehydrate it by the use of a stream of dry hydrochloric acid gas at 100° or 120°. The weighed substance in the bottom of a tared test-tube was placed in an oil-bath at the desired temperature, exposed to a stream of dry hydrochloric acid gas, and weighed at intervals. After thirty minutes of this treatment at 100° the loss was insignificant, while at 120°, on the contrary, rapid decomposition ensued.

An attempt was then made to use a method of dehydration, described by Fischer,[1] by means of which he succeeded in dehydrating pseudouric acid in a synthesis of uric acid. Two-tenths gram of sulphamidomethylpyromucic acid was mixed with 2 grams of powdered anhydrous oxalic acid in a small tube and heated in an oil-bath for twenty-five minutes from 155° to 185°, then ten minutes more at 190°. The oxalic acid sublimed in large part, and a small amount of the substance melted in the bottom of the tube. Upon cooling, solvents were tried, with the idea of separating from the mass any anhydride if formed, but neither benzol, chloroform, nor carbonic disulphide gave an extract.

From these different experiments it seems necessary to conclude that sulphamidomethylpyromucic acid shows no tendency to form an anhydride of the sulphinide form.

Baric Sulphamidomethylpyromucate, $Ba(C_6H_6NSO_5)_2.3H_2O$. —This salt was obtained before the free acid, as has been described above. It is readily soluble in hot water, rather sparingly in cold, and crystallizes in prickly, spherical masses like burrs or sea-urchins, made up of very short, fine needles. The air-dried salt contains 3 molecules of water, which are given off very slowly over sulphuric acid. The salt, heated to 160°, becomes anhydrous.

I. 1.4826 grams air-dried salt gave 0.5757 gram $BaSO_4$.

II. 3.6688 grams air-dried salt lost, at 160°, 0.3289 gram H_2O.

III. 2.8468 grams air-dried salt lost, at 160°, 0.2567 gram H_2O.

	Calculated for $Ba(C_6H_6NSO_5)_2.3H_2O$.	Found. I.	II.	III.
Ba	22.91	22.86	....	....
H_2O	9.02	....	8.97	9.02

I. 0.5205 gram salt, dried at 160°, gave 0.2257 gram $BaSO_4$.

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[1] Ber. d. chem. Ges., 28, 2474.

II. 0.4433 gram salt, dried at 160°, gave 0.1893 gram $BaSO_4$.

	Calculated for $Ba(C_6H_6NSO_5)_2$.	Found. I.	II.
Ba	25.18	25.52	25.13

Calcic Sulphamidomethylpyromucate could not be prepared as a solid, owing to its extraordinary solubility in water. Three and three-tenths grams of sulphamidomethylpyromucic acid were boiled with an excess of calcic carbonate, and the filtered solution evaporated to a volume of from 3 to 4 cc. Although containing 3.5 grams of calcium salt, the solution deposited no crystals even after standing in the cold for twelve hours.

Plumbic Sulphamidomethylpyromucate, $Pb(C_6H_6NSO_5)_2$.—This salt was made by boiling an aqueous solution of the acid with plumbic carbonate. It contained crystal water, but the number of molecules was not determined on account of its extremely rapid efflorescence. Two attempts to dry the salt as rapidly as possible between filter-paper under pressure gave widely varying amounts of crystal water. The salt, moreover, exposed to the air of the room could not be made constant, as it rapidly gained or lost weight with different conditions of temperature and humidity. The salt, dried over sulphuric acid, lost nothing upon being heated to 160°. The solubility of the salt is slight in cold water, but is considerably increased by heat. It crystallizes in clusters of long, slender prisms, which rapidly turn to a powder when exposed to the air. It exhibits a strong tendency to form a basic salt which is practically insoluble in water. For example, it was found impossible to recrystallize the anhydrous salt, as when treated with water it would dissolve but very slightly, a light insoluble substance being formed; yet if a small amount of free acid were added, solution easily took place. The basic salt was also formed, if evaporation was carried too far in crystallizing the salt.

I. 0.7595 gram salt, dried at 160°, gave 0.3737 gram $PbSO_4$.

II. 0.9240 gram salt, dried at 160°, gave 0.4546 gram $PbSO_4$.

	Calculated for $Pb(C_6H_6NSO_5)_2$.	Found. I.	II.
Pb	33.63	33.62	33.61

Argentic Sulphamidomethylpyromucate, $AgC_6H_6NSO_5$.—This salt was prepared by adding the calculated amount of argentic nitrate to the potassium salt of sulphamidomethylpyromucic acid. Both salts were dissolved in a very small amount of hot water and allowed to stand in the dark for twelve hours, at the end of which time an abundance of beautiful clusters of small, thin prisms had been formed. These were filtered, dried by exposure to the air of the room, and were evidently anhydrous, for heated to 100°, the loss in weight was insignificant. It was accompanied, however, with a slight change of color to brown, so that it seemed advisable to carry the heat no higher.

0.6202 gram salt gave 0.3714 gram AgBr.

	Calculated for $AgC_6H_6NSO_5$.	Found.
Ag	34.58	34.40

Potassic Sulphamidomethylpyromucate, $KC_6H_6NSO_5.H_2O$.—This salt was prepared from the calcium salt, above mentioned, by precipitation with potassic carbonate. It is readily soluble in cold water, but the solubility is considerably increased by heat. It crystallizes in long, slender prisms with oblique ends, which contain 1 molecule of water. These show a marked tendency to collect in clusters. The hydrous salt is permanent in the air, but loses water very slowly over sulphuric acid, and becomes anhydrous when heated to 125°, increasing very considerably in volume, so that the heating must not take place in too small a dish. There are not any signs of decomposition accompanying this phenomenon, as the salt, after being heated at 125° for seven hours, was perfectly white, although very light and powdery.

I. 2.6050 grams air-dried salt lost, at 125°, 0.1836 gram H_2O.

II. 2.0205 gram air-dried salt lost, at 125°, 0.1401 gram H_2O.

	Calculated for $KC_6H_6NSO_5.H_2O$.	Found. I.	II.
H_2O	6.89	7.05	6.93

I. 0.8319 gram salt, dried at 125°, gave 0.2935 gram K_2SO_4.

II. 0.6045 gram salt, dried at 125°, gave 0.2154 gram K_2SO_4.

	Calculated for $KC_6H_6NSO_5$.	Found. I.	II.
K	16.09	15.85	16.00

ACTION OF BROMINE.

β-Sulphamido-δ-methylbromfurfurane.

Bromine readily oxidizes a cold aqueous solution of any of the salts of sulphamidomethylpyromucic acid with the evolution of carbonic dioxide. The principal product of the reaction varies with the amount of bromine used; with 1 molecule it is sulphamidomethylbromfurfurane, and the reaction is expressed as follows:

$$CH_3.SO_2NH_2.C_4HOCOOK + Br_2 = CH_3.SO_2NH_2.C_4HBrO + KBr + CO_2.$$

For the preparation of this furfurane compound a cold saturated solution of the barium salt was placed in a small flask, and by means of a pump a slow current of air was drawn first through the calculated amount of bromine, and then into the solution. The speed of the stream carrying the bromine vapor was regulated to a considerable degree by the rapidity with which the color of the bromine was bleached by the solution. Two or three hours generally elapsed before the whole was added, and during this time the absorption of the bromine was watched and made as complete as possible by frequently shaking the flask and retarding the air stream if necessary.

No baric sulphate was formed, as was to be expected, from what is already known concerning the behavior of bromine toward substituted sulphopyromucic acids, since work done by one of us with Palmer,[1] Hendrixson,[2] and Jennings[3] has shown that the sulpho group is retained, when bromine and water act on β-sulphopyromucic acids, but that sulphuric acid is formed from δ-sulphopyromucic acids under these conditions.

Before a very large part of the bromine had been added the sulphamidomethylbromfurfurane, which is sparingly soluble in cold water, began to crystallize out of the solution, and when all the bromine had been added this crystalline precipitate was filtered from the mother-liquor. The yields obtained in preparing this substance were rather low, being usually about 50 per cent of the theoretical amount. The product obtained, however, was very pure, often snow-white, with the correct melting-point without recrystallization, and always possessing less color than the salt from which it was made. In preparing a sample for analysis the first product melted at 123°. This was recrystallized twice from water without altering the melting-point. (The substance often melted under water before dissolving, but came out of solution in solid form.) A small amount of the substance was then recrystallized twice from chloroform, but the melting-ing-point was not changed. Analyses gave the following results:

I. 0.2229 gram substance gave, on combustion, 0.2025 gram CO_2 and 0.0563 gram H_2O.

II. 0.2445 gram substance gave, by the Carius method, 0.1917 gram AgBr and 0.2451 gram $BaSO_4$.

III. 0.2305 gram substance gave 0.1806 gram AgBr and 0.2285 gram $BaSO_4$.

	Calculated for $C_5H_6NBrSO_3$.	Found. I.	II.	III.
C	25.00	24.78	....	....
H	2.52	2.82	....	....
Br	33.30	....	33.36	33.34
S	13.35	....	13.77	13.61

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[1] This JOURNAL, **10**, 413 (1888).

[2] *Ibid.*, **15**, 156 (1893).

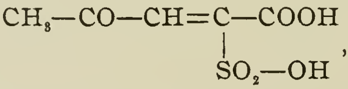
[3] *Ibid.*, **15**, 175 (1893).

β-Sulphamido-δ-methylbromfurfurane melts at 123°. It is sparingly soluble in cold water, much more readily in hot, and is a beautifully crystalline substance. If a hot aqueous solution is cooled rapidly, the substance separates in broad prisms with blunt pointed ends, often in clusters. If the solution is allowed to cool slowly these prisms are very much increased in length. It is easy, by allowing a hot saturated solution to cool even in a 5-centimeter watch-glass, to obtain this substance in very fine needles from 1 to 2 cm. long. In cold alcohol this furfurane compound is extremely soluble, yet it is possible to obtain crystals from an alcoholic solution which are very different from those just described, as they are short, irregular prisms, sometimes almost cubes. It is sparingly soluble in cold benzol, or chloroform, but its solution is considerably increased by heat. In the case of ether, heat makes 1 ittledifference ; it is readily soluble in it hot or cold. In carbonic disulphide it dissolves with great difficulty. An aqueous solution of sulphamidomethylbromfurfurane is neutral to litmus, and does not decompose carbonates, yet the substance dissolves with great ease in cold, dilute, sodic or potassic hydrate solutions, although sparingly soluble in cold water. No ammonia is given off from such solutions even on boiling, and mineral acids reprecipitate the original substance. In a rough quantitative experiment, over 75 per cent of the compound used was precipitated by dilute sulphuric acid after five hours' boiling with a 15 per cent sodic hydrate solution. This behavior indicated that sulphamidomethylbromfurfurane possessed the properties of a weak acid, and must be capable of forming salts.

To a small amount of the furfurane compound, dissolved in cold alcohol, was added a standardized alcoholic potash solution in the proportion of 1 molecule of each substance. In the course of a few seconds a crystalline precipitate appeared, and after standing a short time this was filtered out and dried by pressure between filter-paper. This body contained potassium and was extremely soluble in water, so much so that it could not be recrystallized from an aqueous solution, nor was it precipitated by the addition of alcohol. From hot absolute alcohol it crystallized in irregular, leafy plates. To an aqueous solution of this potassium salt was added a solution of argentic nitrate, when the silver salt separated as a white, curdy precipitate, which proved to be practically insoluble in water. On account of lack of time, a more complete investigation of the salts of this furfurane compound could not be made. That the hydrogen in the sulphamido group is replaced by metal there can be little doubt, as analogous bodies have been described by Jackson and Wing[1] and Wolkow.[2] Potassic permanganate rapidly oxidizes sulphamidomethylbromfurfurane even in the cold, but as yet the products of the reaction have not been identified.

Action of Bromine on Methylsulphamidobromfurfurane or Action of Bromine in Excess on Salts of Sulphamidomethylpyromucic Acid.

As stated above, when a salt of sulphamidomethylpyromucic acid is treated with aqueous bromine, the product obtained depends upon the amount of bromine used. The furfurane compound just described is easily attacked by bromine, so that if a sufficient amount is added, this first product is decomposed and only the results of more complete oxidation obtained. Although the products of this secondary reaction have been examined only in a qualitative way, little doubt is left concerning what takes place. No sulphuric acid is formed even on boiling. If, however, the acid solution be boiled until the carbonic dioxide is expelled, and baric hydrate then added, a heavy, flocculent precipitate is thrown down which is soluble in hydrochloric acid and reprecipitated by ammonia. This is undoubtedly the barium salt of sulphoacetacrylic acid,



$$CH_3\text{—}CO\text{—}CH\text{=}\underset{\substack{|\\ SO_2\text{—}OH}}{C}\text{—}COOH,$$

since, under similar conditions, Palmer and one of us,[3] working with δ-brompyromucic acid, obtained baric sulphofumarate. That the NH_2 group is eliminated is shown by the fact that ammonic bromide is found in quantity in the filtrate from the insoluble barium salt. It is probable, moreover, that the oxidation does not stop with the acetacrylic derivative, as was shown by the following experiment: A small amount of bromine was quickly weighed in a tared test-tube partly full of water, and to this was added a quantity of sulphamidomethylpyromucic acid (neutralized with sodic carbonate), such that there would be 2 molecules of bromine to each molecule of the acid. Immediately after mixing, the contents of the tube were well shaken, when there was an immediate heavy precipitate of the bromfurfurane compound, which later did not dissolve completely. The color of the solution in ten seconds became faint yellow and in ten minutes had entirely disappeared. At the end of an hour there was obtained by filtration from the solution 30 per cent of the amount of sulphamidomethylbromfurfurane, which should be obtained theoretically from the weight of acid used, under the best conditions, that is with 1 molecule of bromine.

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[1] This JOURNAL, 9, 340 (1887).

[2] Ztschr. für Chem., 1870, 323.

[3] This JOURNAL, 10, 414 (1888).

It follows from this, as there was so much unoxidized furfurane compound that the bromine must attack the acetacrylic derivative to a certain extent. On the other hand, although there was, as just shown, a considerable amount of the furfurane body left unaltered after 2 molecules of bromine had been absorbed, yet in the earlier experiments, before 1 molecule had been introduced by the slow air-stream, acetacrylic acid was formed, and at the end of the preparations, in which 1 molecule of bromine had been used, a considerable amount of acetacrylic acid was always present. This fact, of course, is one reason for a low yield.

From the above it is seen that this action of bromine upon salts of sulphamidomethylpyromucic acid consists by no means in the conversion of all the acid into the furfurane body, and then of this latter into sulphoacetacrylic acid, and finally of the oxidation of this compound, but rather, that all three of these reactions are to a certain extent progressing at the same time. On account of these facts, in preparing the bromfurfurane, it was convenient, after a large part of the bromine had been added, to filter and observe the action of more bromine on the filtrate.

Derivatives of δ-Monochlorpyromucic Acid.

After the completion of the work already described on derivatives of methylpyromucic acid, it seemed desirable to investigate the behavior of other substituted pyromucic acids under similar treatment. For this purpose the preparation of δ-chlorpyromucic acid, and from it of β-sulpho-δ-chlorpyromucic acid was next undertaken. The monochlor derivative was made according to the method of L. L. Jackson and one of us.[1] Dry pyromucic acid was dissolved in a flask in one and two-thirds times its weight of absolute alcohol, and to this solution was added a quantity of sulphuric acid (sp. gr. 1.84) equal in weight to that of the pyromucic acid used. After heating for four hours on the steam-bath, the mixture was well cooled and then diluted with five or six times its volume of ice-cold water. The oil which separated was thoroughly washed, first with dilute sodic carbonate solution and then with water, cooled until it crystallized, filtered, and dried by exposure to the air. This crude ester was then distilled before treatment with chlorine. The yield of distilled ester amounted to from 94 to 97 per cent of the weight of acid used. This is an increase of over 10 per cent on the yield which Jackson and one of us obtained. The cause of this was the use of ice-water for the dilution of the alcoholic solution, and also the fact that the solution was well cooled with ice during the washing process and before the filtration of the crystallized ester. Proof of this was obtained by cooling with ice a solution filtered at a higher temperature, when an additional amount of ester was precipitated.

For the formation of the chlor acid, the ester was melted in a small tared flask and heated to 145° by means of an oil-bath. Through the melted ester was passed a stream of dry chlorine. The flask containing the ester was weighed from time to time and the process continued until the ester had absorbed 30 per cent of its weight of chlorine. After cooling, it was then slowly poured into three or four times its weight of a very concentrated alcoholic solution of sodic hydrate, the mixture cooled, well stirred, and after standing several hours the sparingly soluble sodic chlorpyromucate was filtered off. To recover the small amount of sodium salt in solution, the filtrate was saturated with carbonic dioxide, the sodic carbonate removed, and the alcoholic solution evaporated to dryness. This, together with the main portion of sodium salt, was dissolved in hot water and the δ-chlorpyromucic acid precipitated by hydrochloric acid.

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[1] This JOURNAL, 12, 26 (1890).

This crude acid melted at about 165°, did not crystallize in the characteristic leafy form, and therefore contained undoubtedly other chlorpyromucic acids, from which it was separated by a method proposed by L. L. Jackson and one of us,[1] depending upon the fact that baric δ-chlorpyromucate is much more soluble than the barium salts of the other chlorpyromucic acids. The volume of water necessary to keep in solution the baric δ-chlorpyromucate formed, and that necessary to prevent after acidification the precipitation of the small amount of dichlor acids left in the filtrate, was readily calculated from the solubility determinations made by Jackson and one of us. The crude acid was suspended in water, neutralized with ammonia, and the solution of the ammonium salt diluted to twelve times the weight of the acid taken. One-quarter of its weight of crystallized baric chloride was then added, the mixture well stirred, and the sides of the beaker scratched with a rod. After the beaker had stood twenty-four hours, the sparingly soluble barium salts, which had precipitated, were removed by filtration, and the solution was diluted with 25 per cent of its volume of water, heated to boiling, and the chlorpyromucic acid precipitated by acidification. The acid thus obtained, although melting at 168°—8° below the proper melting-point—crystallized in the characteristic leafy plates which showed that it contained but a slight amount of impurity. From 275 grams of ester there were obtained 136.8 grams of acid, or 48 per cent of the theoretical amount. A little of the acid, twice recrystallized from benzol, melted at 176°, the melting-point of pure δ-chlorpyromucic acid. For the preparation of the sulphonic acid, however, it was not thought necessary to recrystallize the whole amount.

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[1] This JOURNAL, **12**, 27 (1890).

β-Sulpho-δ-chlorpyromucic acid was prepared as described by Hendrixson and one of us.[1] δ-Chlorpyromucic acid was slowly added to four times its weight of fuming sulphuric acid, the mixture being well stirred and cooled. It dissolved more quickly and with less evolution of heat than methylpyromucic acid, and the solution was much lighter colored in this case. The mixture was allowed to stand in a desiccator twenty-four hours, then largely diluted with water and neutralized with baric carbonate, the excess of which, together with the baric sulphate, was removed by filtration. The solution of the barium sulphonate was precipitated with potassic carbonate, the baric carbonate removed, and the filtered solution evaporated to very small volume. On cooling this solution, the potassium salt crystallized out, the weight of which amounted to nearly twice that of the chlorpyromucic acid used, or 95 per cent of the theoretical yield.

β-Sulphamido-δ-chlorpyromucamide.

Potassic sulpho-δ-chlorpyromucate is anhydrous.[2] Accordingly, 25 grams of the powdered salt which had stood for some time over sulphuric acid were mixed in a small boiling-flask with a little more than 2 molecules of finely divided phosphoric pentachloride, about 38 grams, the mixing of the two substances being accomplished merely by shaking the flask. Heat was soon developed, and in a short time almost complete liquefaction took place. In order to complete the reaction, however, the flask was heated in an oil-bath at 110° for three hours, after which most of the phosphoric oxychloride was distilled off under diminished pressure, and when the flask had cooled its pasty contents were shaken out into a beaker containing 200 cc. of cold water. The inorganic potassium salts soon dissolved and the oil which separated was washed in a separating-funnel. The phosphoric oxychloride which remained dissolved in the acid chloride was decomposed very slowly by cold water and its complete removal was not attempted, but after several washings the oil was converted directly into the amide by dropping it slowly into a beaker containing 150 cc. of ice-cold strong ammonia, the mixture being well stirred as the reaction progressed. The ammoniacal solution was allowed to stand in a covered beaker twenty-four hours. It was then poured into a shallow crystallizing dish, where it remained until the ammonia had completely evaporated. Hot water was then added to dissolve the solid, the solution cooled, and the amide which crystallized out filtered off. This first product usually contained some ammonic chloride and was somewhat dark-colored, but upon crystallization and treatment with bone-black the salt was colorless and free from ammonic chloride. The weight of sulphamido-δ-chlorpyromucamide thus obtained was about 12 grams, or 65 per cent of the theoretical amount.

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[1] This JOURNAL, **15**, 151 (1893).

[2] *Ibid.*, **15**, 154 (1893).

In the case of the corresponding methyl compound, it will be remembered, 1 molecule of phosphoric pentachloride was used with practically a quantitative yield of the acid chloride. In this case 1 molecule was at first tried, but the low yields of amide obtained, together with the presence of unaltered potassic sulphochlorpyromucate, even after treatment with phosphoric pentachloride for four hours at 160°, showed that conversion of the potassium salt into the chloride was far from complete. Two molecules were therefore used with much better results, as described above. There was another remarkable difference of behavior observed in the preparation of these two amides. In preparing the methyl compound it was not necessary to wait for the complete evaporation of the ammonia before dissolving the amide. After standing twenty-four hours the residual ammonia was expelled by heat, whereas it was found in the case of the chlor compound that such treatment greatly reduced the yield. In one preparation the solution, which had been allowed to stand for some time but which was by no means free from ammonia, was transferred to a flask and immediately boiled with boneblack for some hours, and although this was the customary treatment in the case of the methyl compound, the yield with the chlor acid was less than one-third the usual amount of amide. Complete spontaneous evaporation of the ammonia at the temperature of the room gave the best results.

The product obtained after treatment with boneblack melted at about 211° and retained a slight yellow color. For analysis a few grams were twice recrystallized from water. The amide then melted at 212°. Further recrystallization of a small amount, using alcohol as the solvent, did not alter the melting-point, nor did it remove the trace of color. The analyses gave the following results :

I. 0.2042 gram substance gave, on combustion, 0.1977 gram CO_2 and 0.0487 gram H_2O.

II. 0.2184 gram substance gave 0.2130 gram CO_2 and 0.0471 gram H_2O.

III. 0.1902 gram substance gave, by the Carius method, 0.1194 gram AgCl and 0.1993 gram $BaSO_4$.

IV. 0.2321 gram substance gave 0.2397 gram $BaSO_4$.

	Calculated for $C_5H_5N_2ClSO_4$.	Found.			
		I.	II.	III.	IV.
C	26.72	26.41	26.60	....	....
H	2.24	2.67	2.41	....	....
Cl	15.78	....	....	15.53	....
S	14.27	....	....	14.39	14.18

These analyses show that the compound is a double amide corresponding completely to the methyl compound already described, and not a sulphinide such as would be formed by the parallel reaction in the benzol series.

β-Sulphamido-δ-chlorpyromucamide is very sparingly soluble in cold water or cold alcohol, but either of these solvents, boiling, dissolves it readily, water the more freely, still in hot water it is less soluble than the corresponding methyl compound. In chloroform, ether, carbonic disulphide, or benzol the substance is insoluble. From a hot aqueous solution it crystallizes in short, thick prisms, usually with pointed ends, but sometimes rectangular. If the solution is allowed to cool slowly and quietly, the substance is deposited in large clusters of exceedingly short, stout needles. It melts at 212°.

β-Sulphamido-δ-chlorpyromucic Acid.

Ammonia was evolved from this amide even by the action of a cold solution of baric hydrate, but as the action was slow in the cold, the experiments were carried on at the boiling-point. A cold, saturated solution of baric hydrate was mixed with a quantity of the amide in sufficient volume to give 3 molecules of baric hydrate to each molecule of the amide, and the solution was boiled for two or three hours, at the end of which time the amount of ammonia evolved from the solution had become very slight, and this seemed the best point for stopping the action as it was found that a boiling baric hydrate solution also decomposes the sulphamido group together with the furfurane ring, although only to a limited extent. That such a decomposition of the ring was taking place was shown by the formation of a precipitate in the solution as the boiling continued, which was proved to consist of baric sulphite, carbonate, and oxalate. In order to learn to what extent this total destruction of the molecule took place, this precipitate was filtered out, washed, and then treated in a flask with very dilute hydrochloric acid and bromine, with due care that no sulphurous dioxide should escape. From the weight of baric sulphate obtained it was calculated that about 6 per cent of the amide was usually totally destroyed. This same decomposition was shown to take place when *β*-sulpho-*δ*-chlorpyromucate was boiled with baric hydrate, and was apparently more rapid in this case than with the sulphamide. After seventeen hours' boiling with 3 molecules of baric hydrate, 5 grams of this barium salt gave, after the treatment described above, 1.86 grams of baric sulphate, which showed that 71 per cent of the salt had been entirely decomposed. The filtrate was proved to contain considerable amounts of carbonic dioxide and oxalic acid.

The barium salt, which was the principal product of the action of baric hydrate on the amide, was obtained as in the case of the corresponding methyl compound. The weight of air-dried salt amounted to one and one-fourth times that of the amide used. The loss of nitrogen in the form of ammonia from the double amide during the formation of this body showed that it was the salt either of the sulphinide or the sulphamido acid. A sample of it was recrystallized several times, the barium removed by precipitation with sulphuric acid, and the crystals, which separated upon evaporation of the filtrate, still further purified by recrystallization. Their melting-point was 194°. The substance, which was perfectly white, was dried *in vacuo* and analyzed with the following results:

I. 0.2178 gram substance gave, on combustion, 0.2109 gram CO_2 and 0.0387 gram H_2O.

II. 0.3152 gram substance gave 18.3 cc. moist N at 22° and 743 mm. pressure.[1]

	Calculated for		Found.	
	$C_5H_4NClSO_5$.	$C_5H_2NClSO_4$.	I.	II.
C	26.60	28.91	26.40	....
H	1.79	0.97	1.99	....
N	6.22	6.76	....	6.57

These results prove that the δ-chlor double amide, like the methyl compound, gives with baric hydrate salts of sulphamido-δ-chlorpyromucic acid, not of a sulphinide, like those in the benzol series.

The sample of acid analyzed melted, it has been said, at 194°. A small amount of the substance mixed with solid baric hydrate on a watch-glass and moistened with water gave no ammonia that could be detected with turmeric paper, even after gentle warming and long standing. Yet neither this fact nor the analytic results were considered sufficient proof that it was absolutely free from amide in very small traces, which might affect the melting-point. The case was very different from that of the methyl compound where the amide was much more easily decomposed, and where a large excess of baric hydrate could be used without fear of great reduction of the yield. To find a method for complete purification of the acid was not so easy, since the amide was more insoluble in alcohol or water than the acid and in other common solvents the acid was insoluble. It was found, however, somewhat later, that the potassium salt of this acid, although very soluble in water, was precipitated from a concentrated aqueous solution by alcohol, whereas the amide dissolved in water cannot be precipitated in this way. A sample of the potassium salt, which gave no ammonia with concentrated baric hydrate in the cold, was dissolved in water and precipitated by alcohol. This process was repeated five times. From this purified potassium salt was made the silver salt by precipitation with argentic nitrate, and this silver salt, being sparingly soluble in water, was recrystallized from rather a large volume of it. The free acid was then separated by hydrochloric acid and the melting-point observed. It was 194° to 195°. After this thorough purification there was no possibility of the presence of an impurity of amide. The sample was, however, recrystallized from water several times with no change of the melting-point. The melting-point of the substance used for analysis was consequently only a fraction of 1° low.

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[1] The nitrogen determination given above was made after the usual fashion with a tube filled with cupric oxide. After the analysis was well under way it was noticed that Menschutkin ("Analytical Chemistry," p. 488) states that the use of plumbic chromate is necessary in the case of substances containing sulphur, to prevent the reduction of carbonic dioxide to its monoxide by the sulphurous acid formed. The nitrogen, after it had been measured, was accordingly treated with cuprous chloride, and as this caused no diminution in its volume, this accident had not occurred in this case.

β-Sulphamido-δ-chlorpyromucic acid melts at 194° to 195°, and is readily soluble even in cold water; its solubility, however, is increased by heat. From an aqueous solution it crystallizes in rectangular prisms which are often slender and clustered. It is exceedingly soluble even in cold alcohol. In ether it dissolves with great difficulty. It is practically insoluble in carbonic disulphide, chloroform, or benzol.

Although the methyl acid corresponding to this body had shown no tendency to form a sulphinide, two attempts were made to dehydrate this chlor-substance. 0.2571 gram of the acid was heated in a small tube by means of an oil-bath for half an hour at a temperature of 195° to 197°, that is just above its melting-point. The substance blackened somewhat during this treatment, but crystallized on cooling, and melted only 4° below its original melting-point. Carbonic disulphide, chloroform, or benzol, dissolved mere traces of this product, as they did of the original acid. The loss in weight, due probably to slight decomposition, was only 0.0039 gram, or 19 per cent of the weight of 1 molecule of water. 0.3082 gram of the substance contained in a boat placed in a glass tube was heated by means of an air-bath to 120° for three-quarters of an hour, then to 170° for the same length of time, and during the period of heating a rapid stream of hydrochloric acid was passed through the tube. A loss in weight of 2 milligrams was observed which amounted to only 8 per cent of a molecule of water. The substance had turned slightly gray in color, but its melting-point was unaltered. From this work it is apparent that this acid shows no more tendency to lose water than the methyl derivative already examined.

Baric Sulphamido-δ-chlorpyromucate, $Ba(C_5H_3NClSO_5)_2.3H_2O$.—This salt was obtained, as has been said, by the action of baric hydrate directly upon the sulphamidochlorpyromucic amide. It is sparingly soluble in cold water, readily in hot, and crystallizes from a hot solution in masses of small, fine needles, looking like burrs. The tendency to form these aggregations is so great that it is very difficult with the microscope to see any crystalline form—often nothing but small, round lumps can be seen. Moreover, it is hard to free from mother-liquor the crystals which are obtained from the rapid cooling of a hot solution, as they form a kind of paste from which, even with the pump, it is impossible to remove the liquid. Better results are obtained if the solution is allowed to cool slowly and quietly. The salt containing 3 molecules of water is permanent in the air. It begins to lose weight very slowly over sulphuric acid, but quickly becomes anhydrous when heated to 110°.

I. 3.0054 grams air-dried salt lost, at 110°, 0.2521 gram H_2O.

II. 2.0848 grams air-dried salt lost, at 110°, 0.1759 gram H_2O.

	Calculated for $Ba(C_5H_3NClSO_5)_2.3H_2O$.	Found. I.	II.
H_2O	8.43	8.39	8.44

I. 0.9188 gram salt, dried at 110°, gave 0.3660 gram $BaSO_4$.

II. 0.6999 gram salt, dried at 110°, gave 0.2790 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3NClSO_5)_2$.	Found. I.	II.
Ba	23.43	23.45	23.46

Calcic Sulphamido-δ-chlorpyromucate, $Ca(C_5H_3NClSO_5)_2.6H_2O$(?).—The calcium salt was made by boiling a solution of the acid with calcic carbonate and evaporating the filtrate to very small volume. On cooling and allowing the solution to stand for some time the salt, which is very soluble even in cold water, began to crystallize out. It crystallizes in rectangular prisms, often so short as to appear cubical, which sometimes, strangely enough, have very slightly concave ends. The salt was separated from the mother-liquor by rapid filtration on the pump, and remained in the funnel only two or three minutes, when it was well dried by pressure between filter-paper and immediately pulverized and weighed. The weighed salt, on exposure to the air, lost weight, at first, rapidly. During the first hour and a half 1.8743 grams of the salt lost 0.0603 gram, while in the next six hours the loss was only 0.0006 gram, and after that this rate of loss continued, decreasing somewhat toward the end of the six weeks the experiment lasted. As it would have taken too much time to bring it to a constant weight in the air, it was next tried over sulphuric acid when the rate of loss was somewhat increased, but after a few days the substance was heated and soon became constant in weight at 145°, and, as an analysis showed, anhydrous.

1.8743 grams salt, dried between filter-paper, lost, when heated to 145°, 0.3368 gram H_2O.

	Calculated for $Ca(C_5H_3NClSO_5)_2.6H_2O$.	Found.
H_2O	18.09	17.97

This analysis does not settle the amount of water of crystallization definitely, as it may be that the water lost so rapidly in the first ninety minutes was not water of crystallization but hygroscopic moisture. In that case the salt contains 5 molecules of water.

Calculated.	Found.
15.55	15.25

0.5254 gram salt, dried at 145°, gave 0.1438 gram $CaSO_4$.

	Calculated for $Ca(C_5H_3NClSO_5)_2$.	Found.
Ca	8.18	8.05

Plumbic Sulphamido-δ-chlorpyromucate, $Pb(C_5H_3NClSO_5)_2.H_2O$.—This salt was made by boiling a solution of the acid with an excess of plumbic carbonate, filtering, and evaporating. It is very sparingly soluble in cold water, somewhat more readily in hot, and does not show a tendency to form a basic or insoluble anhydrous salt like the corresponding methyl compound. It crystallizes from a hot aqueous solution if cooled quickly in broad, flat, irregular plates. If the solution cools slowly, however, none of this variety appears, but loose clusters of long, thin prisms are obtained. The hydrous salt was permanent in the air and over sulphuric acid. Heated to 140°, it lost a weight corresponding to 1 molecule of water.

I. 2.8785 grams air-dried salt lost, at 140°, 0.0804 gram H_2O.

II. 3.0959 grams air-dried salt lost, at 140°, 0.0849 gram H_2O.

	Calculated for $Pb(C_5H_3NClSO_5)_2.H_2O$.	Found. I.	Found. II.
H_2O	2.67	2.79	2.74

I. 0.6128 gram salt, dried at 140°, gave 0.2830 gram $PbSO_4$.

II. 0.8652 gram salt, dried at 140°, gave 0.3958 gram $PbSO_4$.

	Calculated for $Pb(C_5H_3NClSO_5)_2$	Found. I.	Found. II.
Pb	31.53	31.53	31.25

Argentic Sulphamido-δ-chlorpyromucate, $AgC_5H_3NClSO_5$.—This salt was made by adding to a hot solution of the potassium salt the calculated amount of argentic nitrate. The salt separated at once. For analysis it was recrystallized from a hot solution. It is sparingly soluble in cold water, more readily in hot, and crystallizes in rectangular prisms and plates, which are usually grouped together in irregularly shaped masses. The air-dried crystals are anhydrous, losing no weight in three hours at 110°.

0.4652 gram air-dried salt gave 0.2006 gram AgCl.

	Calculated for $AgC_5H_3NClSO_5$.	Found.
Ag	32.46	32.46

Potassic Sulphamido-δ-chlorpyromucate, $KC_5H_3NClSO_5$.—This salt was prepared by neutralizing the free acid with potassic carbonate. Although dissolving freely in cold water its solubility is increased by heat. It crystallizes in beautiful rectangular prisms, usually three or four times as long as broad, but sometimes these are shortened into broad plates, and occasionally become perfectly square. They are rarely grouped in clusters. A very insignificant loss in weight took place upon heating the air-dried salt for three hours at 160°. It was evidently, therefore, anhydrous.

I. 0.5617 gram air-dried salt gave 0.1830 gram K_2SO_4.
II. 0.7536 gram air-dried salt gave 0.2452 gram K_2SO_4.

	Calculated for $KC_5H_3NClSO_5$.	Found. I.	II.
K	14.84	14.63	14.61

Considerable difficulty was encountered in oxidizing this salt for analysis without serious loss of substance. Determination (I) was made by dissolving the salt in a mixture of very dilute sulphuric and nitric acids and slow evaporation on the steam-bath, followed by very careful heating with a ring-burner. In analysis (II), the salt was dissolved in water, bromine added to precipitate the furfurane compound (this reaction is described below) and the filtrate, after driving off the excess of bromine, evaporated in platinum, followed by treatment with sulphuric acid in a crucible. This method was no more satisfactory than the first, as the furfurane compound which had been dissolved by the necessary washing showed the same tendency to spatter in burning.

Action of Bromine and Water. β-Sulphamido-α,α-chlorbromfurfurane.

With bromine, salts of sulphamido-δ-chlorpyromucic acid show a behavior similar to that, already described, of the salts of the corresponding methyl acid. With equal molecules of acid and bromine a bromfurfurane compound is obtained with the evolution of carbonic dioxide. Seven grams of anhydrous barium salt were dissolved in water and by means of a slow current of air 3.8 grams of bromine were introduced. No baric sulphate was formed. The crystalline precipitate was filtered from the mother-liquor and amounted to 5.2 grams, or 85 per cent of the theoretical yield. This substance melted at 130° to 131° and contained a small amount of sulphamidochlorpyromucamide, shown by the formation of ammonia with baric hydrate in the cold, but this was due to the fact that a sample of barium salt had been used which was not entirely free from that body. Owing to its insolubility in cold water and rapid increase of solubility with heat, the furfurane compound was purified by two recrystallizations from large volumes of hot water, when it melted at 134° to 135° and contained no amide. This melting-point was not altered by two more crystallizations from hot water and three from chloroform. The analyses gave the following results :

I. 0.2062 gram substance gave, on combustion, 0.1383 gram CO_2 and 0.0303 gram H_2O.

II. 0.2468 gram substance gave, by the Carius method, 0.3145 gram $AgCl + AgBr$ (which yielded 0.4455 gram AgI), and 0.2239 gram $BaSO_4$.

	Calculated for $C_4H_3NClBrSO_3$.	Found. I.	II.
C	18.42	18.29	....
H	1.16	1.64	....
Cl + Br	44.29	....	44.39
Cl	13.61	....	13.57
Br	30.68	....	30.86
S	12.30	....	12.46

After the Carius determination the mixture of argentic chloride and bromide was dissolved from the Gooch mat with a little strong potassic cyanide solution, three or four times the theoretical amount of potassic iodide was added, after which the cyanide was decomposed, and all the silver precipitated as iodide by the addition of dilute sulphuric acid.

β-Sulphamido-α,α-chlorbromfurfurane melts at 134° to 135°. It is sparingly soluble in cold water, readily soluble in hot, and crystallizes from a hot aqueous solution in clusters of long needles even if rapidly cooled in a watch-glass. If a large volume is allowed to cool slowly, magnificent, long needles result. It is extremely soluble even in cold alcohol, and it is with difficulty that crystals can be obtained from an alcoholic solution. Such crystals, however, are very different in appearance from those from the aqueous solution, as they are small, irregular, thick prisms. It is not very soluble in ether, hot or cold. In hot chloroform or benzol it dissolves moderately freely, separating in the form of fine needles as the solution cools. Carbonic disulphide dissolves it but sparingly.

Sulphamidochlorbromfurfurane, like the methyl compound already described, acts as a weak acid, being readily dissolved by cold solutions of the alkalies and precipitated by mineral acids. The potassium salt, which is extremely soluble in water, was prepared by the addition of alcoholic potash to the furfurane compound dissolved in alcohol. After a few minutes the salt crystallized from this solution and was filtered out and recrystallized from absolute alcohol. It separated in shining, irregular scales. An aqueous solution of argentic nitrate was added and the silver salt was precipitated in the form of compact masses of small, fine needles. It is very insoluble even in hot water. These compounds were not analyzed, but they undoubtedly correspond to the salts prepared from the methylfurfurane body and probably have the metal attached to nitrogen in the SO_2NH_2 group.

The formation of sulphamidochlorbromfurfurane from sulphamidochlorpyromucic acid with 1 molecule of bromine corresponds to the behavior of the methyl acid described above, and this similarity also extends to the action with more bromine, as with this the furfurane body in question is oxidized, no sulphuric acid is formed, and baric hydrate, after the expulsion of the carbonic dioxide, gives a heavy, flocculent precipitate soluble in hydrochloric acid and reprecipitated by ammonia. Although this body has not been analyzed, there is no doubt that it is the baric sulphofumarate obtained first by Palmer and one of us[1] and later by Hendrixson and one of us.[2]

Derivatives of δ-Monobrompyromucic Acid.

In making the δ-monobrompyromucic acid the method of preparation given by Sanger and one of us[3] was followed except in a few details. Dry pyromucic acid was treated with the vapor of bromine at 100°. For 20 grams of pyromucic acid a half-liter Erlenmeyer flask was used, provided with a return-condenser and a drop-funnel, the end of which entered the mouth of a test-tube resting upon the bottom of the flask and serving to catch the liquid bromine. The bottom of this test-tube had been blown out and flattened so that more surface would be heated for the volatilization of the liquid, and a large hole had been blown in its side 2 cm. from the bottom, through which the bromine vapor might escape.

The powdered acid, mixed with glass beads in order to present more surface to the action of the bromine, was placed on the bottom of the flask and heated on the steam-bath. For 20 grams of acid 36 grams of bromine were used, and its introduction required about three hours. By the end of two more hours the bromine was completely absorbed; the acid was then dissolved in boiling water, and filtered in a steam-funnel. Upon cooling, the solution deposited about 60 per cent of the theoretical amount of δ-brompyromucic acid. This first product melted at about 177°. In order to free it from dibrompyromucic acids a method was resorted to similar to that employed for the purification of the chlor compound, which depended upon the insolubility of the barium salts of the dibrom acids. The product was dissolved in forty times its weight of water, one-tenth of its weight of baric chloride added, the solution allowed to stand for some time, and the barium salts of the sparingly soluble dibrom acids filtered off. Upon acidification of the filtrate the acid separated in leafy plates which melted at 180°, and was sufficiently pure for the preparation of the sulphonic acid. β-Sulpho-δ-brompyromucic acid and its salts have been made and described by Palmer and one of us.[1] Dry δ-brompyromucic acid was slowly stirred into three and one-half times its weight of fuming sulphuric acid while the beaker containing the mixture was cooled. Solution took place quickly and the amount of color developed was slight, as was the case with the δ-chlor compound. The solution was allowed to stand twenty-four hours before dilution; baric carbonate was then added to neutralization, and the filtered solution precipitated with potassic carbonate. The baric carbonate was filtered off and the solution of the potassium salt evaporated and crystallized. Somewhat over 90 per cent of the theoretical yield of potassium salt was obtained.

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[1] This JOURNAL, **10**, 414 (1888).

[2] *Ibid.*, **15**, 156 (1893).

[3] Proc. Am. Acad., **21**, 138; Ann. Chem. (Liebig), **232**, 42.

β-Sulphamido-δ-brompyromucamide.

It was attempted to prepare sulphamido-δ-brompyromucamide from potassic sulphobrompyromucate by the action of phosphoric pentachloride and ammonia, in the same manner in which the corresponding methyl and chlor compounds had been made. One or two attempts showed that while there was undoubtedly δ-bromamide formed, yet there was also produced in no very small quantity the δ-chlor compound, which has already been described. The presence of potassic bromide in the reaction flask, together with the dark-red color which the acid chloride assumed was enough to prove that part of the bromine in the δ-position on the furfurane ring was set free and replaced by chlorine. The product of the reaction after one recrystallization was tested qualitatively for chlorine. About 0.2 gram of the substance was mixed with sodic carbonate and potassic nitrate, oxidized in a hot crucible, fused with potassic dichromate, and submitted to the chromic oxychloride test for chlorine. More than a trace was present. As it would evidently be a useless task to attempt to purify this bromamide, owing to the similarity of the properties of the two bodies, this method of preparation was abandoned.

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[1] This JOURNAL, **10**, 408 (1888).

Phosphorous terbromide was next tried on a small scale with unsatisfactory results. Three molecules of the potassium salt (3 grams) were treated with two of phosphorous terbromide (1.7 grams) for two hours at 130°. After treatment with water an oil separated which, with ammonic hydrate, yielded nothing resembling the expected amide, but instead, 0.7 gram of a light-brown powdery substance, which was practically insoluble in water and melted at 122°. Unfortunately, owing to lack of time, this body could not be investigated.

Attention was then turned to phosphoric pentabromide. This substance was prepared from equal molecules of phosphorous terbromide and bromine. The bromine was allowed to drop slowly from a burette into the terbromide contained in a mortar. The mixture was well stirred at first with a rod and then powdered with a pestle as it became solid. The pentabromide was removed to a bottle and a stream of dry air passed through it to remove any excess of bromine. Thus prepared, the pentabromide remained dry and powdery, and could be weighed out for use with little difficulty. With it satisfactory results were obtained by the following method: The potassium salt was mixed in a dry boiling-flask with a little over 2 molecules of pentabromide and the mixture heated in an oil-bath. At 70° the contents of the flask liquefied. The temperature was kept at 90° from two to three hours, when the flask was allowed to cool, and its dark-red, viscous contents poured into a beaker of cold water. After a vigorous stirring, during which some heat was developed by the decomposition of the phosphoric oxybromide, the beaker was cooled with water, whereupon the oil solidified, and the wash-water was removed by decantation. The bromide was melted and stirred with water at about 30°, then cooled again, and the water decanted from the solid. This washing of the bromide as an oil and decantation of the wash-water after solidification was continued until the solid bromide lost its red color and became light yellow and the wash-waters contained no bromine and only slight amounts of hydrobromic acid.

The treatment of the solid acid bromide with ammonic hydrate resembled in all respects that of the liquid acid chloride of chlorpyromucic acid recently described. The ammonia was ice-cold, small amounts of substance were slowly introduced, the solution was well stirred during the reaction, and then allowed to stand until the ammonia had completely volatilized. Upon treatment with hot water there remained insoluble a small amount of a light-brown substance which resembled the product obtained with phosphorous terbromide. From this the solution was filtered, evaporated, and allowed to cool, when it deposited the amide in crystalline form, the weight of which amounted to 50 per cent of the theoretical yield. The melting-point of this product once recrystallized was 200° to 201°, which was not altered by three recrystallizations from water, but the substance did not fuse sharply. A sample was analyzed with the following results:

I. 0.2072 gram substance gave, on combustion, 0.1697 gram CO_2 and 0.0360 gram H_2O.

II. 0.2713 gram substance gave, by the Carius method, 0.1900 gram AgBr and 0.2372 gram $BaSO_4$.

	Calculated for $C_5H_5N_2BrSO_4$.	Found. I.	II.
C	22.30	22.33	....
H	1.87	1.95	....
Br	29.70	....	29.80
S	11.91	....	12.00

These analytic results show that here too a sulphinide has not been obtained, but that the substance is sulphamidobrompyromucamide. Yet, as the melting-point was not sharp, it must have contained an amount of impurity which could not be detected by analysis, but was sufficient to affect seriously the melting-point.

As the substance melted no more sharply after two more crystallizations from water, alcohol was tried as a solvent, when, after two crystallizations, the substance began to melt at 201°, but was not completely liquefied until the temperature reached 219°. Four more crystallizations from the same solvent gave the melting-point 219° to 220°, which is undoubtedly the fusing-point of the pure substance, since it was not changed by two final crystallizations. The yield of the final purified product was small. There was enough, however, to make a halogen determination.

0.1331 gram substance gave, by the Carius method, 0.0931 gram AgBr.

	Calculated for $C_5H_5N_2BrSO_4$.	Found.
Br	29.70	29.75

β-Sulphamido-δ-brompyromucamide melts at 219° to 220°, and is sparingly soluble in cold water or alcohol; with heat it dissolves readily in these solvents. In ether, chloroform, carbonic disulphide, or benzol it is insoluble. From an aqueous solution quickly cooled it crystallizes in small, short, rectangular prisms. If a dish containing a hot solution is allowed to cool slowly, the crystallized substance presents a peculiar aspect, as it appears in lines of hard, hemispherical lumps, 2 or 3 mm. in diameter, clinging to the glass and radiating from the centre of the dish. Sometimes with the aid of a lens short, thick, spike-like points can be seen projecting from these masses.

Since the compound just described was proved by analysis to be analogous to the chlor and methyl double amides previously investigated, another instance of difference in behavior between benzol and furfurane derivatives had been found.

β-Sulphamido-δ-brompyromucic Acid.

In order to study the behavior of this double amide with baric hydrate, 8.3 grams of amide were boiled in a flask with a solution of baric hydrate in the proportion of 3 molecules of hydrate to each molecule of the amide. The treatment was continued three hours, during which time the formation of a precipitate occurred in the solution, showing decomposition of the furfurane ring, as was the case in the similar treatment of the chlor compound. At the end of the boiling ammonia was slowly evolved, also showing decomposition. The amount of baric sulphite formed was determined as before, and showed total decomposition of 7.5 per cent of the amide. The alkaline solution, after filtration, was treated with carbonic dioxide, again filtered and evaporated, 9 grams of barium salt crystallized from the solution on cooling. This salt gave off no ammonia in one hour with cold baric hydrate and was therefore free from amide. It was, however, thrice recrystallized, the barium precipitated by sulphuric acid, and the crystals of acid obtained from the filtrate purified by recrystallizing them six times from water. After the third time the melting-point remained constant at 190° to 191°. The substance was dried *in vacuo* and analyzed :

I. 0.2560 gram substance gave, on combustion, 0.2057 gram CO_2 and 0.0460 gram H_2O.

II. 0.1560 gram substance gave, by the Carius method, 0.1079 gram AgBr.

	Calculated for		Found.	
	$C_5H_4NBrSO_5$.	$C_5H_2NBrSO_4$.	I.	II.
C	22.21	23.81	21.92	....
H	1.49	0.80	2.01	....
Br	29.59	31.72	....	29.44

These analyses show that the substance is sulphamidobrompyromucic acid and not the sulphinide. The 9 grams of barium salt obtained in the process just described amounted to 80 per cent of the theoretical yield.

β-Sulphamido-δ-brompyromucic acid melts at 190° to 191°. The acid is readily soluble even in cold water, and is extremely soluble in alcohol. It crystallizes in long, thin, rectangular prisms, which usually appear in clusters of slender needles. In ether it is very sparingly soluble, and practically insoluble in chloroform, carbonic disulphide, or benzol.

That it shows no more tendency to form an anhydride than did the corresponding methyl and chlor acids was made evident by the following work : 0.1668 gram of the acid was heated for three-quarters of an hour at 193° to 195°. The substance blackened somewhat, but crystallized on cooling, melted only 4° below the proper melting-point, and the loss in weight of 0.0030 gram corresponded to but 27 per cent of a molecule of water. Chloroform, benzol, or carbonic disulphide dissolved nothing from the residue. The acid was therefore practically unchanged. Heating the substance for two hours at 170° in a rapid current of dry hydrochloric acid gas had a similar effect. The melting-point was lowered 4°, the color of the body changed from pure white to a light gray, and the loss in weight amounted to only 20 per cent of 1 molecule of water.

Baric Sulphamido-δ-brompyromucate, $Ba(C_5H_3NBrSO_5)_2.3H_2O$.—This salt was obtained directly from the amide by the action of baric hydrate, as has been described. It was purified by recrystallization from water. It is very readily soluble in hot water, sparingly in cold. It is deposited from a hot solution in small, round masses of fine needles looking like sea-urchins. The air-dried salt is permanent in the air and contains 3 molecules of water, which begins to escape slowly over sulphuric acid. The salt quickly becomes anhydrous at 130°. It was analyzed with the following results:

I. 3.0575 grams air-dried salt lost, at 130°, 0.2308 gram H_2O.

II. 2.4456 grams air-dried salt lost, at 130°, 0.1838 gram H_2O.

	Calculated for $Ba(C_5H_3NBrSO_5)_2.3H_2O$.	Found.	
		I.	II.
H_2O	7.41	7.55	7.51

I. 0.7015 gram salt, dried at 130°, gave 0.2428 gram $BaSO_4$.

II. 0.6371 gram salt, dried at 130°, gave 0.2206 gram $BaSO_4$.

	Calculated for $Ba(C_5H_3NBrSO_5)_2$.	Found.	
		I.	II.
Ba	20.34	20.37	20.38

The calcium salt, like that of the corresponding methyl acid, was found to be too soluble in water for investigation. A solution of the acid, boiled with calcic carbonate, filtered, and evaporated to very small volume, deposited nothing even after several hours standing.

Plumbic Sulphamido-δ-brompyromucate, $Pb(C_5H_3NBrSO_5)_2.2H_2O$.—This salt was prepared by boiling an aqueous solution of the acid with plumbic carbonate. The filtered solution was evaporated and allowed to cool, whereupon the salt which is sparingly soluble in cold water began to crystallize from the solution. It was deposited in peculiar shuttle-shaped crystals, usually short with pointed ends and curving sides. Occasionally they were longer with straight parallel sides, but the ends, as before, curving and pointed. These crystals often occur in clusters. The air-dried salt was twice obtained for analysis by crystallization, contained 2 molecules of water and was permanent in the air. Once, a salt with less water was obtained, which was probably due to crystallization from solution at a higher temperature. The air-dried salt loses its 2 molecules of water almost completely when placed for a few days over sulphuric acid. A very small additional loss in weight was noted upon heating to 145°.

I. 1.9397 grams air-dried salt lost, over sulphuric acid, 0.0861 gram, and in addition 0.0015 gram at 145°.

II. 1.8167 grams air-dried salt lost, over sulphuric acid, 0.0833 gram, and in addition 0.0003 gram at 145°.

	Calculated for $Pb(C_5H_3NBrSO_5)_2.2H_2O$.	Found. I.	II.
H_2O	4.61	4.52	4.60

I. 0.5994 gram salt, dried at 145°, gave 0.2433 gram $PbSO_4$.

II. 0.7833 gram salt, dried at 145°, gave 0.3173 gram $PbSO_4$.

	Calculated for $Pb(C_5H_3NBrSO_5)_2$.	Found. I.	II.
Pb	27.77	27.72	27.67

Argentic Sulphamido-δ-brompyromucate, $AgC_5H_3NBrSO_5.1\frac{1}{2}H_2O$.—The silver salt was prepared by the precipitation of a concentrated solution of the potassium salt with argentic nitrate. The salt was dissolved in hot water, filtered, and recrystallized. It is very sparingly soluble in cold water, but dissolves readily with heat, and crystallizes in short, thick prisms which are not quite rectangular. The air-dried salt, which contains 1.5 molecules of crystal water, is permanent in the air, but over sulphuric acid slowly loses weight, and when heated to 110° quickly becomes anhydrous.

I. 2.2394 grams air-dried salt lost, at 110°, 0.1476 gram H_2O.

II. 1.4611 grams air-dried salt lost, at 110°, 0.978 gram H_2O.

	Calculated for $AgC_5H_3NBrSO_5.1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	6.69	6.59	6.69

0.8050 gram salt, dried at 110°, gave 0.4006 gram AgBr.

	Calculated for $AgC_5H_3NBrSO_5$.	Found.
Ag	28.62	28.58

Potassic Sulphamido-δ-brompyromucate, $KC_5H_3NBrSO_5.H_2O$. —The potassium salt was made by the action of potassic carbonate on the solution of the calcium salt described above. The filtered solution was evaporated to very small volume when, upon cooling, the potassium salt crystallized out. It separates from solution in very slender, rectangular prisms, which are almost invariably loosely clustered. The air-dried salt contains 1 molecule of water, which it does not lose over sulphuric acid, but it becomes anhydrous when heated to 160°.

I. 2.3727 grams air-dried salt lost, at 160°, 0.1336 gram H_2O.

II. 1.9753 grams air-dried salt lost, at 160°, 0.1108 gram H_2O.

	Calculated for $KC_5H_3NBrSO_5.H_2O$.	Found. I.	II.
H_2O	5.52	5.63	5.61

I. 0.6731 gram salt, dried at 160°, gave 0.1872 gram K_2SO_4.

II. 0.3930 gram salt, dried at 160°, gave 0.1113 gram K_2SO_4.

	Calculated for $KC_5H_3NBrSO_5$.	Found. I.	II.
K	12.70	12.49	12.71

Action of Bromine and Water. β-Sulphamido-α,α-dibromfurfurane.

The behavior of aqueous bromine with the salts of sulphamido-δ-brompyromucate is entirely analogous to its behavior, already described, with the salts of the corresponding chlor compound. Five grams of anhydrous baric sulphamido-δ-brompyromucate were dissolved in water and treated by means of an air-stream with 2.4 grams of bromine vapor—1 molecule for each furfurane ring. At the end of two hours the addition of the bromine was completed and there were filtered from the solution 3.7 grams of crystalline precipitate. This substance melted at 148° to 150°, and represented 85 per cent of the theoretical yield of the furfurane compound. It was recrystallized three times from about 200 cc. of water. After the first crystallization the melting-point was 153°.5, and neither the last two crystallizations from water nor subsequent trials with benzol or chloroform altered it. An analysis gave the following results:

I. 0.2135 gram substance gave, on combustion, 0.1221 gram CO_2 and 0.0245 gram H_2O.

II. 0.2649 gram substance gave, by the Carius method, 0.3253 gram AgBr.

	Calculated for $C_4H_3NBr_2SO_3$.	Found. I.	II.
C	15.74	15.60	....
H	0.99	1.28	....
Br	52.43	....	52.26

β-Sulphamido-α,α-dibromfurfurane melts at 153°.5. It is very insoluble in cold water, more readily soluble in hot, and crystallizes from a hot solution in very long, thin, obliquely terminated prisms, usually in clusters. The substance is very soluble even in cold alcohol, but crystallizes from a hot solution in small, thick prisms, rather irregular in shape. In ether it is somewhat soluble, and also in hot chloroform, from which it crystallizes, on cooling, in fine needles. In hot benzol it is readily soluble, sparingly in cold. The substance is practically insoluble in carbonic disulphide.

The feeble acid properties of the sulphamido group appear in this compound, and it is readily soluble in alkalies and precipitated by acids. The potassium salt was precipitated by the addition of alcoholic potash to an alcoholic solution of the furfurane body. This salt, recrystallized from absolute alcohol, appeared in beautiful, shining scales. From an aqueous solution of this the crystalline silver salt was precipitated with aqueous argentic nitrate. The potassium salt is extremely soluble in water, the silver salt practically insoluble.

Sulphamidodibromfurfurane was easily oxidized in cold aqueous solution by bromine with the formation of the same sulphofumaric acid which was obtained by the oxidation of the chlorbrom compound. After an excess of bromine had been added and the carbonic dioxide expelled, it was found that sulphuric acid was absent, but that baric hydrate produced the voluminous, flocculent precipitate, characteristic of sulphofumaric acid.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF POTASSIC NITRITE ON MUCOBROMIC ESTER.[1]

By H. B. Hill and O. F. Black.

The products formed by the action of alkaline nitrites upon mucobromic acid, which were first described by Hill and Sanger[2] in 1882, have been repeatedly the subject of investigation in this laboratory during the past few years.[3] A product of an entirely different nature, which they obtained by the action of potassic nitrite upon ethyl mucobromate, has not been further described. Its formula was shown at the time to be $KC_6H_6NO_6$, but no reactions were discovered which gave definite proof of its structure. A few years later Mr. W. S. Hendrixson made a preliminary study of the body and obtained some interesting results, but he was unable to bring the investigation to a definite conclusion before his departure from Cambridge. We are indebted to him for certain experimental material, which we shall describe later.

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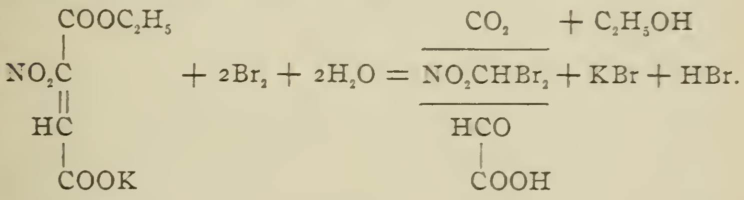
[1] The work described in this paper was done under the supervision of Professor Hill, but the paper was written after his untimely death. C. L. J.

[2] Ber. d. chem. Ges., **15**, 1910 (1882).

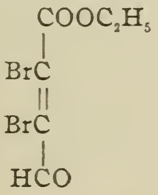
[3] This Journal, **22**, 89; **24**, 1. Ber. d. chem. Ges., **33**, 1241.

The structure of the compound $KC_6H_6NO_6$ was determined by studying the action of bromine and water upon it, which decomposed it, giving an oil identified as dibromnitromethane and glyoxylic acid, which was detected in the aqueous liquid by conversion into its phenylhydrazone identified by analysis. As it was possible that this glyoxylic acid might have proceeded from the oxidation of the ethyl group of the ethyl mucobromate, the experiment was repeated with the corresponding salt, $KC_5H_4NO_6$, made from methyl mucobromate, and, as this also gave glyoxylic acid when treated with bromine and water, it follows that this acid results from a breaking up of the molecule of the new acid. This decomposition proves that the substance is potassic ethylnitromaleate, as shown by the following reaction :

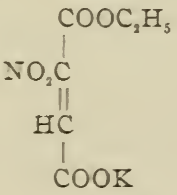


$$\begin{array}{l}COOC_2H_5\\ \quad|\\ NO_2C\\ \quad\|\\ HC\\ \quad|\\ COOK\end{array} + 2Br_2 + 2H_2O = \begin{array}{c}CO_2\\ \hline NO_2CHBr_2\\ \hline HCO\\ |\\ COOH\end{array} \begin{array}{l}+ C_2H_5OH\\ + KBr + HBr.\\ \\ \\ \\ \end{array}$$

The relation of this potassic ethylnitromaleate to the ethyl mucobromate, from which it is formed, is made evident by the following formulas :

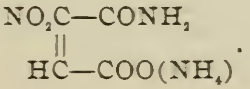


$$\begin{array}{l}COOC_2H_5\\ \quad|\\ BrC\\ \quad\|\\ BrC\\ \quad|\\ HCO\end{array}$$



$$\begin{array}{l}COOC_2H_5\\ \quad|\\ NO_2C\\ \quad\|\\ HC\\ \quad|\\ COOK\end{array}$$

The structure thus determined for this compound was confirmed by the study of the action of ammonia upon it, which formed the amide

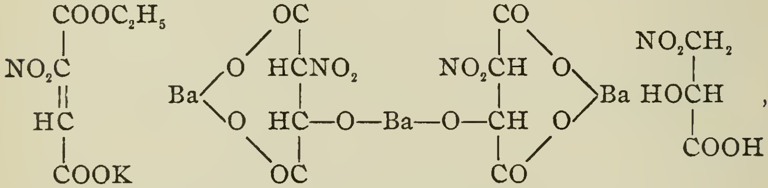


$$\begin{array}{l}NO_2C—CONH_2\\ \quad\|\\ HC—COO(NH_4)\end{array}.$$

Several of the salts derived from this amido acid were made and analyzed.

The potassic ethylnitromaleate is, in some respects, a remarkably stable substance, as it was not decomposed even by evaporation to dryness with strong hydrochloric acid, and all attempts to convert it into salts with other metals than potassium failed. We did, however, succeed in making an ammonium and an aniline salt, the latter of which was analyzed.

When the potassic ethylnitromaleate in aqueous solution was treated with baric hydrate a voluminous precipitate was formed, which was not the ethylnitromaleate but the salt of another acid, since the addition of dilute hydrochloric acid decomposed it with evolution of carbonic dioxide and formation of nitrolactic acid. Its formation from the potassic ethylnitromaleate on the one hand, and its conversion into nitrolactic acid on the other, indicate that it is a basic baric nitromalate formed by the addition of water to the nitromaleate,



but the percentage of barium in such a salt is 53.87, whereas our analyses gave results varying from 54.68 to 56.45 per cent of barium. This, however, should not lead to the rejection of this theory, since this excess of barium was undoubtedly caused by the presence of some baric carbonate, which could hardly be avoided in a precipitate formed from baric hydrate with the salt of such an unstable acid and incapable from its nature of purification. Another theory in regard to this salt was that it consisted of a mixture of baric carbonate and baric nitrolactate, which would explain its behavior with acids as well as the theory that it was a nitromalate. To decide between these theories we determined the number of molecules of baric hydrate necessary to form the salt from each molecule of potassic ethylnitromaleate. If it was a mixture of carbonate and nitrolactate 2 molecules would be necessary ; if it was a nitromalate, one and a half. As a matter of fact, 1.635 molecules of baric hydrate were found to be necessary. There is no doubt, therefore, that the salt is the basic baric nitromalate.

Nitrolactic acid (α-oxy-β-nitropropionic acid),

$$H_2CNO_2CHOHCOOH,$$

was formed by the action of dilute hydrochloric acid on the basic baric nitromalate, carbonic dioxide being evolved. The composition of the nitrolactic acid, which melts at 76° to 77°, was determined by its analysis and an analysis of its silver salt. With baric hydrate the nitrolactic acid formed a pinkish-white precipitate, which gave percentages of barium on analysis about 2 per cent too high for the formula

$$(CH_2NO_2CHOCOO)Ba.$$

We ascribe these results to a slight amount of baric carbonate in the precipitate, as in the case of the basic baric nitromalate discussed above, for, although the calculated amount of barium would agree fairly with that found, if we assumed the formation of an anhydride by the removal of 1 molecule of water from two of the basic salt, such an assumption seems inadmissible in this case, because the salt gives unaltered nitrolactic acid on acidification.

The acetnitrolactic acid, $H_2CNO_2HCOC_2H_3OCOOH$, and its silver salt were made and analyzed.

The nitrolactic acid contains an unsymmetrical atom of carbon, and we accordingly studied its action toward polarized light. Our experiments, which did not go beyond the preliminary stage, showed that an active acid could be obtained which showed a specific laevo rotation of about 20°.

The constitution of the nitrolactic acid was determined by reducing it with tin and hydrochloric acid, which converted it into isoserin (β-aminolactic acid), $CH_2NH_2CHOHCOOH$, recognized by its characteristic copper salt,[1] $C_3H_5O_3NCu$, and by a determination of its solubility which agreed with that of a specimen made by us from β-chlorlactic acid and also with that determined by Melikoff[1] for isoserin. Our acid is therefore the α-oxy-β-nitropropionic acid.

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[1] Emil Fischer and Leuchs : Ber. d. chem. Ges., **35**, 3787 (1902).

EXPERIMENTAL PART.

The mucobromic acid used in this work was prepared by the method of Simonis,[2] that is, oxidizing furfurol with water and an excess of bromine. The mucobromic ethyl ester was made from this by warming the acid for several hours on the steam-bath with about three times its weight of alcohol containing 3 per cent of hydrochloric acid, after which the excess of alcohol was evaporated off and the residue poured into cold water. The brown crystalline mass thus obtained was purified by dissolving it in hot alcohol and bringing the solution to crystallization by plunging it in a freezing-mixture of ice and salt. The yield was 90 per cent of the weight of acid. The ester was also made by mixing equal weights of mucobromic acid and alcohol and strong sulphuric acid and allowing the mixture to stand in the cold.

Potassic Ethylnitromaleate, $C_2NO_2HCOOKCOOC_2H_5$.—Fifteen grams of the mucobromic ethyl ester were dissolved in 105 cc. of alcohol mixed with 42 cc. of water, and to this was added a solution of 22 grams of potassic nitrite also dissolved in a mixture of 105 cc. of alcohol with 42 cc. of water. The mixture was allowed to stand two or three days, during which time light-green crystals of the salt were gradually deposited, which were dried *in vacuo* and analyzed with the following results :

I. 0.5028 gram salt gave, on combustion, 0.5800 gram CO_2 and 0.1264 gram H_2O.

II. 0.7925 gram salt gave, on combustion, 0.9134 gram CO_2. The water was lost. In both these combustions the salt was mixed with chromic oxide.

III. 0.7358 gram salt gave 43.5 cc. moist N_2 at 20°.5 and 759.5 mm. pressure.

IV. 0.6381 gram salt gave 36.25 cc. moist N_2 at 19° and 775 mm. pressure.

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[1] Ber. d. chem. Ges., **13**, 1266.

[2] *Ibid.*, **32**, 2084 (1899).

V. 0.6417 gram salt gave 0.2445 gram K_2SO_4.

VI. 0.5091 gram salt gave 0.1943 gram K_2SO_4.

	Calculated for $KC_6H_6NO_6$.	Found. I.	II.	III.	IV.	V.	VI.
C	31.71	31.45	31.44	....	....	....	....
H	2.64	2.81	....	....	....	....	....
N	6.17	....	....	6.47	6.37	....	....
K	17.22	....	....	....	....	17.10	17.14

The yield of potassic ethylnitromaleate was 60 per cent of the weight of mucobromic ester taken.

Properties of Potassic Ethylnitromaleate.—It crystallizes in colorless, clustered, flat prisms, which are sparingly soluble in cold water, more readily in hot water, and its solution, when boiled, develops an acid reaction. One part of it dissolves in 21.6 parts of water at 16°. It is somewhat soluble in boiling strong alcohol and can be recrystallized from dilute alcohol. It is a remarkably stable body, since evaporation to dryness with strong hydrochloric acid on the steam-bath produced no appreciable decomposition and all attempts to make salts with other metals from it by double decomposition failed, although the ammonium and aniline salts were obtained.

The aniline salt was prepared as follows: Ten grams of the potassium salt were treated with 200 cc. of water, 35 cc. of strong hydrochloric acid, and 5.8 grams of aniline dissolved in 15 cc. of hydrochloric acid and 10 cc. of water. The salt was purified by three recrystallizations from alcohol and analyzed with the following results:

I. 0.2278 gram salt gave, on combustion, 0.4249 gram CO_2 and 0.1086 gram H_2O.

II. 0.2572 gram salt gave 23.1 cc. moist N at 24° and 771 mm. pressure.

	Calculated for $C_2HNO_2COOC_2H_5COOHC_6H_5NH_2$.	Found. I.	II.
C	51.07	50.87	....
H	4.96	5.30	....
N	9.93	....	10.24

Potassic Methylnitromaleate, $C_2NO_2HCOOKCOOCH_3$.—This substance was made by treating the mucobromic methyl ester with potassic nitrite in dilute alcohol in the way described under the ethyl compound.

I. 0.2470 gram substance gave, on evaporation with strong sulphuric acid, 0.1005 gram K_2SO_4.

II. 0.2505 gram substance gave 0.1023 gram K_2SO_4.

	Calculated for $C_2NO_2HCOOKCOOCH_3$.	Found. I.	Found. II.
K	18.35	18.26	18.33

In its properties it resembles the ethyl compound most closely.

Action of Bromine and Water on Potassic Ethylnitromaleate.

Ten grams of the potassium salt were suspended in water and a stream of air saturated with bromine vapor passed through the mixture, until 2 molecules of bromine (14.08 grams) had been added for each molecule of the salt. During this operation a heavy oil with a penetrating odor separated from the liquid and collected in drops at the bottom of the vessel. After removing it from the water this was dried over calcic chloride and distilled twice, when it boiled from 158° to 163° with partial decomposition. Its analysis gave the following results:

I. 0.3493 gram oil gave, by the Carius method, 0.5874 gram AgBr.

II. 0.3363 gram oil gave 0.5638 gram AgBr.

	Calculated for $CHBr_2NO_2$.	Found. I.	Found. II.
Br	73.07	71.56	71.35

The oil is therefore evidently dibromnitromethane. The yield was good, as 7.6 grams were obtained from 10 grams of the potassic ethylnitromaleate instead of 9.65 grams, that is, 78.8 per cent of the theoretical yield.

The solution from which the dibromnitromethane had been obtained was freed from it completely by neutralization with calcic carbonate and distilling with steam until no more of the oil passed over. The residue was then slightly acidified with hydrochloric acid and treated with a solution of the hydrochloride of phenylhydrazine; the precipitate thus obtained showed the melting-point 136° to 137°, which, although lower than 143° to 145°, that given by von Pechmann for the phenylhydrazone or glyoxylic acid, $C_6H_5NHNCHCOOH$, agrees well with the melting-points given by other observers. That it is this phenylhydrazone is proved by the following analyses:

I. 0.1945 gram substance gave, on combustion, 0.4162 gram CO_2 and 0.0923 gram H_2O.

II. 0.2220 gram substance gave 33.1 cc. N_2 at 24° and 765 mm. pressure.

III. 0.2499 gram substance gave 37.2 cc. N_2 at 23° and 758 mm. pressure.

	Calculated for $C_6H_5NHNCHCOOH$.	Found. I.	II.	III.
C	58.54	58.34	....	....
H	4.88	5.33	....	....
N	17.08	....	16.83	16.72

Glyoxylic acid must therefore have been one of the products of the reaction of bromine on potassic ethylnitromaleate, which may be written as follows:

$$C_2NO_2HCOOKCOOC_2H_5 + 2Br_2 + 2H_2O = CHBr_2NO_2 + C_2H_2O_3 + CO_2 + KBr + HBr + C_2H_5OH.$$

In order to prove that the glyoxylic acid was one of the products of the decomposition of the nitromaleic acid molecule and not formed by oxidation of the ethyl group the experiment was repeated with the potassic methylnitromaleate, and the glyoxylic acid found in this case also.

Action of Ammonia on the Potassic Ethylnitromaleate.

Nitromaleic Amide.—A portion of the potassium salt was dissolved in a solution of ammonic hydrate and allowed to stand at ordinary temperatures for some hours, when it was found that a heavy precipitate of yellowish-white needles had been thrown down, leaving but little organic matter in the solution. These crystals consisted of a mixture of the ammonium and potassium salts of the nitromaleamide,

$$C_2HNO_2CONH_2COOH.$$

Its composition was determined by the analyses of the silver and potassium salts prepared from it, as follows:

Silver Salt, $C_2HNO_2CONH_2COOAg$.—An aqueous solution of the mixed potassium and ammonium salts was treated with argentic nitrate, which threw down a nearly insoluble precipitate made up of minute white crystals; these were dried *in vacuo* and analyzed as follows:

0.3500 gram salt gave 0.2463 gram AgBr.

	Calculated for $C_2HNO_2CONH_2COOAg$.	Found.
Ag	40.45	40.41

Potassium Salt, $C_2HNO_2CONH_2COOK$.—A solution of the free amide was prepared by the cautious addition of hydrochloric acid to the silver salt. It was found that the amide was stable in solution at ordinary temperature, but was decomposed during evaporation to dryness. The potassium salt was made by treating the solution of the free amide with potassic carbonate. It was dried *in vacuo* and analyzed:

I. 0.2463 gram salt gave, on evaporation with sulphuric acid, 0.1061 gram K_2SO_4.

II. 0.2429 gram salt gave 0.1043 gram K_2SO_4.

	Calculated for $C_2HNO_2CONH_2COOK$.	Found. I.	II.
K	19.73	19.35	19.27

The potassium salt forms white crystals very sparingly soluble in water whether hot or cold.

Ammonium Salt, $C_2HNO_2CONH_2COONH_4$.—This salt was made by allowing the aniline salt to stand for two or three days with a solution of ammonic hydrate. It gave the following results on analysis:

0.2517 gram substance gave, on combustion, 0.2528 gram CO_2 and 0.1002 gram H_2O.

	Calculated for $C_2HNO_2CONH_2COONH_4$.	Found.
C	27.11	27.39
H	3.95	4.42

It crystallizes in fine, white needles and is more soluble than the potassium salt.

Action of Baric Hydrate on Potassic Ethylnitromaleate.

Baric Nitromalate.—When a solution of potassic ethyl nitromaleate was treated with baric hydrate and enough baric chloride to replace the potassium, a new insoluble barium salt was formed which was evidently derived from another acid, since on the addition of hydrochloric acid carbonic dioxide was evolved and nitrolactic acid formed. The study of this salt offered great difficulties, because it could not be recrystallized owing to its insolubility, and the acid, as was just stated, decomposes as soon as set free. We could find no way, therefore, to purify it, and have analyses only of the salt as precipitated. These gave results varying from 52.17 to 53.40 per cent of barium in the air-dried salt and from 54.68 to 56.45 per cent in the salt dried at 100°. This variation indicates that the crude precipitate was contaminated with baric carbonate, which could hardly be avoided in a precipitate made with baric hydrate from a salt that decomposes with great ease into a carbonate and nitrolactate. The most probable formula for this barium salt, considering its relation to the nitromaleic acid on the one side and the nitrolactic on the other is $Ba_3(C_4H_2NO_7)_2$, a basic baric malate. The percentage of barium calculated for this formula is not far from those found.

	Calculated for $Ba_3(C_4H_2NO_7)_2$.	Found.
Ba	53.87	54.68–56.45

In view of its behavior with hydrochloric acid it was possible that this barium salt might be a mixture of nitrolactate formed directly from the nitromaleate and baric carbonate. This theory, however, was excluded by determining the amount of baric hydrate necessary to form the salt when baric hydrate alone was used. If it were the mixture of nitrolactate and carbonate, 2 molecules of baric hydrate would be necessary to each molecule of the potassic ethylnitromaleate, but in an actual experiment only 1.635 molecules were used in the complete formation of the salt, that is, the amount required to form the basic baric malate. This formula, therefore, can be adopted as the one which best represents the known facts.

β-Nitrolactic Acid, $CH_2NO_2CHOHCOOH$.—When the barium salt described in the preceding section was treated with dilute hydrochloric acid it dissolved with evolution of carbonic dioxide. The solution thus obtained was then treated with ether in a continuous extractor for three or four hours, and the extract, which consisted of a colorless mass of crystals, was purified by crystallization from ether and chloroform until it showed the constant melting-point 76° to 77°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.2101 gram substance gave, on combustion, 0.2041 gram CO_2 and 0.0750 gram H_2O.

II. 0.1955 gram substance gave 0.1912 gram CO_2 and 0.0690 gram H_2O.

III. 0.1820 gram substance gave 16.8 cc. moist N_2 at 15°.5 and 766 mm. pressure.

	Calculated for $CH_2NO_2CHOHCOOH$.	Found.		
		I.	II.	III.
C	26.67	26.50	26.67	....
H	3.70	3.96	3.92	....
N	10.37	....	....	10.82

Properties of β-Nitrolactic Acid.—It crystallizes from ether and chloroform in small, irregular, white prisms, which melt at 76° to 77° (uncorr.). It is very soluble in water, alcohol, or ether; more sparingly soluble in chloroform. As this nitrolactic acid contains an unsymmetrical carbon atom, a preliminary attempt was made to resolve it into its optically active isomers. Seven grams of the acid were converted into its strychnine salt, which was then recrystallized from hot water until two successive filtrates gave a constant angle, when tested in the polariscope. The salt thus obtained was dissolved in water, acidified with hydrochloric acid, and the active nitrolactic acid extracted with ether. 0.3494 gram of this acid gave a laevo rotation of 0°.69, which corresponds to a specific rotation of about 20°.

Argentic Nitrolactate, $CH_2NO_2CHOHCOOAg$.—An aqueous solution of nitrolactic acid was warmed gently with an excess of argentic carbonate and filtered hot, when, on cooling, the silver salt crystallized from the filtrate. It was dried *in vacuo* and analyzed with the following result:

0.1808 gram salt gave 0.1410 gram AgBr.

	Calculated for $CH_2NO_2CHOHCOOAg$.	Found.
Ag	44.63	44.79

The salt crystallizes from warm water in fine, white needles, which are decomposed by direct sunlight. It is stable in aqueous or acid solutions, but decomposes in presence of alkalies.

Barium Salts of Nitrolactic Acid.—When nitrolactic acid was warmed in aqueous solution with baric carbonate the product was an unmanageable amorphous wax. If, however, an aqueous solution of the acid was treated with baric hydrate, a slightly pinkish precipitate was obtained which gave the following results on analysis:

I. 0.2240 gram substance gave, on evaporation with sulphuric acid, 0.2007 gram $BaSO_4$.

II. 0.2493 gram substance gave 0.2233 gram $BaSO_4$.

III. 0.2414 gram substance gave 0.2160 gram $BaSO_4$.

	Calculated for $(CH_2NO_2CHOCOO)Ba$.	Found.		
		I.	II.	III.
Ba	50.74	52.67	52.66	52.61

The percentages of barium found are decidedly too high, but in a precipitate made with baric hydrate enough baric carbonate might be present to raise the percentages found 2 per cent. Upon acidification the barium salt gives nitrolactic acid, which seems to exclude the formation of an anhydride, or any similar reaction which would give theoretical numbers agreeing more nearly with those found.

Calcic carbonate gave a white crystalline salt when warmed with an aqueous solution of nitrolactic acid.

Acetnitrolactic Acid, $CH_2NO_2CHOC_2H_3OCOOH$.—This substance was prepared by heating nitrolactic acid on the steam-bath for two or three hours with an excess of acetic anhydride. The unaltered acetic anhydride was then evaporated off and the crystalline residue purified by recrystallization from ether and chloroform until it showed the constant melting-point 90° to 91°, when it was dried *in vacuo* and analyzed with the following result:

I. 0.1797 gram substance gave, on combustion, 0.2250 gram CO_2 and 0.0646 gram H_2O.

II. 0.1547 gram substance gave 11.2 cc. moist N_2 at 20°.5 and 768 mm. pressure.

	Calculated for $CH_2NO_2CHOC_2H_3OCOOH$.	Found. I.	Found. II.
C	33.90	34.14	....
H	3.95	3.99	....
N	7.93	....	8.12

The acetnitrolactic acid crystallizes from a mixture of ether and chloroform in large, perfect, white octahedra, freely soluble in water.

Argentic Acetnitrolactate, $CH_2NO_2CHOC_2H_3OCOOAg$.—This salt was obtained by mixing strong aqueous solutions of the acetnitrolactic acid and argentic nitrate, the crystals which separated were washed with water, dried *in vacuo*, and analyzed with the following result:

0.2165 gram substance gave 0.1082 gram AgCl.

	Calculated for $CH_2NO_2CHOC_2H_3OCOOAg$.	Found.
Ag	38.03	37.61

It crystallizes in bunches of gleaming white needles and is decomposed by heating with water, which is strange, as the argentic nitrolactate is stable under these conditions.

The Reduction of Nitrolactic Acid.

Isoserin, $CH_2NH_2CHOHCOOH$.—The nitrolactic acid was heated with tin and strong hydrochloric acid diluted with its own volume of water in a small flask on the steam-bath for two or three hours. The tin was then precipitated by sulphuretted hydrogen and the chloride of the amido compound in the filtrate decomposed with argentic oxide. Finally the silver, which had dissolved, was removed with sulphuretted hydrogen. On concentrating the final filtrate the product was deposited in small, hard crystals, which, dried *in vacuo*, gave the following results on analysis :

I. 0.2098 gram substance gave, on combustion, 0.2612 gram CO_2 and 0.1244 gram H_2O.

II. 0.1835 gram substance gave 21.7 cc. moist N_2 at 17° and 742 mm. pressure.

	Calculated for $CH_2NH_2CHOHCOOH$.	Found. I.	II.
C	34.29	33.95	....
H	6.67	6.59	....
N	13.32	....	13.42

These results showed that the substance was an amidolactic acid, but it remained to be determined whether it was serin, α-amido-β-oxypropionic acid, or isoserin, α-oxy-β-amidopropionic acid. The crystalline form—small, hard, nearly cubic crystals—did not agree with the long, thin, monoclinic prisms, the form assigned to isoserin by Haushofer,[1] and, accordingly, to settle the question we made the copper salt, which Emil Fischer and Leuchs[2] have shown is very characteristic, and also determined the solubility of the free acid.

The copper salt, dried at 100°, gave the following results on analysis :

I. 0.2525 gram salt gave 0.1184 gram cupric oxide.
II. 0.1884 gram salt gave 0.0893 gram cupric oxide.

	Calculated for $C_3H_5O_3NCu$.	Found. I.	II.
Cu	38.10	37.44	37.85

These low results are explained by the observation of Emil Fischer that the copper salt of isoserin retains water even when dried at 110°. Unfortunately, his paper did not reach us until this part of the work was finished, so that we cannot give analyses of thoroughly dried specimens. This, however, is not necessary, as these results prove that the formula is $CuC_3H_5O_3N$, characteristic of the isoserin, and not the salt $Cu(C_3H_6O_3N)_2$ of the serin.

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[1] Jsb., 1880, p. 779.

[2] Ber. d. chem. Ges., **35**, 3787 (1902).

To settle the identity of our substance beyond question we compared its solubility with that of some isoserin made from β-chlorlactic acid, and purified by several recrystallizations, conversion into the copper salt, decomposition with sulphuretted hydrogen, and finally crystallization from hot water. The specimen of isoserin from the nitrolactic acid was purified by careful recrystallization.

I. 7.1943 grams of a solution of isoserin from nitrolactic acid, saturated at 20°, contained 0.1087 gram solid.

II. 8.2879 grams of a solution of isoserin from β-chlorlactic acid, saturated at 20°, contained 0.1251 gram solid.

Parts of water necessary to dissolve one part of isoserin.

I.	II.
65.16	65.27

These results agree with those of Melikoff,[1] who found that 1 part of isoserin dissolves in 65.4 parts of water, whereas 1 part of serin[2] dissolves in 24.7 parts of water. There can be no doubt, therefore, that our substance is isoserin.

A METHOD FOR THE DETERMINATION OF CHLORIC ACID.

By W. S. Hendrixson.

In the methods for the determination of chloric acid by reduction, metallic zinc, in some form, and ferrous sulphate have been the reducing agents most used, though several others, including sulphur dioxide and formic aldehyde, have been employed. The conditions under which zinc and ferrous sulphate have been used have been much varied. Thorpe[3] and Thorpe and Eccles[4] used the zinc-copper couple to reduce chlorates and determined the chloride, resulting from the chlorate, with a solution of silver. Bothamley and Thompson[5] showed that the results by this method were too low unless sulphuric acid was added near the end of the reduction to dissolve any basic salts of zinc. By the same method Becker[1] also found the results too low and preferred to use zinc dust and a little copper sulphate. Fleissner[2] used zinc dust and boiled the solution one hour, but Becker attained complete reduction only by using a large excess of zinc dust with sufficient sulphuric acid to dissolve it completely without the aid of heat.

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[1] Ber. d. chem. Ges., **13**, 1266 (1880).

[2] Erlenmeyer, *Ibid.*, **13**, 1078 (1880); Cramer: J. prakt. Chem., **96**, 94 (1865).

[3] J. Chem. Soc. (London), **11**, 541.

[4] *Ibid.*, **14**, 856.

[5] *Ibid.*, **53**, 164.

Stelling[3] reduced chlorates by long boiling with ferrous sulphate, in alkaline solution, and determined the resulting chloride. Becker found that the reaction was very slow and incomplete, and recommended a neutral solution of ferrous sulphate. Carno[4] reduced the chlorates in bleaching-powder by heating at 100° with a large excess of ammonium ferrous sulphate and an excess of sulphuric acid. The amount of chlorate was found either by titrating the resulting chloride by the method of Volhard or by determining the excess of ferrous sulphate with permanganate. Rosenbaum[5] states that chlorine will be lost in this method of reduction if the acid and the ferrous sulphate are added to a hot solution of the chlorate.

In the course of my work on the action of chloric acid on metals,[6] it was observed that metallic iron very readily reduces free chloric acid even in very dilute solutions. At ordinary room temperature the solution of the metal is very rapid in moderately concentrated solutions of the acid, and the iron goes at once into the ferric condition, as was proved by many tests while solution was going on. No gas is evolved, but the iron simply disappears and there results the yellowish-brown solution of ferric salt, and the solution remains clear if the acid is in considerable excess. Whether iron alone thus reduces chloric acid completely could not be determined with accuracy, owing to the fact that toward the end of the reaction large amounts of oxide and possibly basic salt are necessarily formed, and these make it impracticable to obtain a solution suitable for titration with silver without the use of agents which would also decompose chloric acid. An approximation, however, showed that at least 95 per cent of the chloric acid was reduced. These facts suggested that the determination of chloric acid might be brought to a very simple form by using metallic iron as the chief reducing agent in the presence of an excess of sulphuric acid, which would prevent the formation of insoluble compounds, make the method applicable to chlorates by setting free the chloric acid, and form ferrous sulphate, which is itself a reducing agent for chloric acid, and which would already be present to serve, when oxidized, as the indicator in the titration of the chloride formed, by the method of Volhard. It is evident, therefore, that such a method would be a very simple combination of the two general methods already mentioned, the reduction of chloric acid by a metal, and probably a more efficient one than zinc, and the reduction by ferrous sulphate.

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[1] Repert. anal. Chem., **1**, 377.

[2] Ztschr. anal. Chem., **20**, 115.

[3] *Ibid.*, 6, 32.

[4] Compt. rend., **122**, 449.

[5] Ztschr. angew. Chem., 1893, 80.

[6] J. Am. Chem. Soc., **26**, 747.

To carry out the method a weighed amount of pure potassium chlorate or a measured volume of chloric acid of known strength was placed in a small flask with about 50 cc. of pure sulphuric acid having a concentration of about 10 per cent, and an excess of "card-teeth" used in most laboratories as a convenient form of iron. In some of the experiments recorded below, the flask was fitted with a delivery-tube which dipped into water, the purpose being to prevent the possible loss of hydrochloric acid, a precaution which at room temperature was proved to be wholly unnecessary. At first ferric salt is formed and gives the solution the characteristic color due to ferric salts, but the salt is soon reduced and the solution becomes colorless or slightly green. If all the chlorate is dissolved at the beginning of the experiment, the disappearance of the yellow color may be taken to mark the end of the reduction, which requires, at room temperature, about one hour. No doubt the reduction could be hastened by heating, if precaution were taken to prevent the loss of hydrochloric acid by volatilization. As might naturally be expected, the method serves quite as well for bromic acid and bromates as for chloric acid and chlorates, and two determinations of the bromic acid in potassium bromate are given below.

After the reduction was completed the solution was made up to a definite volume and portions of it were titrated with N/20 silver nitrate by Volhard's method. Usually an excess of silver was added before the iron was oxidized with an excess of nitric acid to the ferric condition to serve as the indicator. There seems, however, to be little danger of the loss of chlorine if the nitric acid is added before the silver.

The following are results obtained by the method described, the amounts of silver required in the titrations being calculated to chloric acid or bromic acid :

1. 5 cc. of a solution of chloric acid gave 1.0639 grams $HClO_3$.
2. 5 cc. of the same solution gave 1.0619 grams $HClO_3$.

The same solution, titrated with standard barium hydroxide gave, in 5 cc., 1.0665 grams $HClO_3$.

3. 0.4595 gram $KClO_3$ gave 0.3158 gram $HClO_3$; calculated, 0.3165 gram.
4. 0.6709 gram $KClO_3$ gave 0.4628 gram $HClO_3$; calculated, 0.4622 gram.
5. 0.8300 gram $KClO_3$ gave 0.5731 gram $HClO_3$; calculated, 0.5718 gram.
6. 1.2744 grams $KClO_3$ gave 0.8778 gram $HClO_3$; calculated, 0.8778 gram.
7. 0.3350 gram $KBrO_3$ gave 0.2605 gram $HBrO_3$; calculated, 0.2585 gram.
8. 1.0983 grams $KBrO_3$ gave 0.8460 gram $HBrO_3$; calculated, 0.8478 gram.

The method above described seems to have some advantages. It is extremely simple. It can be carried out at room temperature, avoiding any danger of the loss of hydrochloric acid by heating. In the reduction and the preparation of the solution for titration are necessary only iron and pure sulphuric and nitric acids, which are always at hand in every laboratory, and no filtering or other operations likely to occasion loss of chlorine or loss of time are required.

Perchloric acid shows the same indifference toward metallic iron as toward most other reducing agents, and does not, therefore, interfere in the determination of chloric acid by this method.

IOWA COLLEGE, GRINNELL, IA.,
March 18, 1904.

Contributions from the Sheffield Laboratory of Yale University.

ON THE SOLUBILITY OF BARIUM AND MERCURIC CHLORIDES.

BY H. W. FOOTE AND H. S. BRISTOL.

A double salt of mercuric and barium chlorides has been described by Bonsdorf,[1] who assigned the formula

$$BaCl_2.2HgCl_2.2H_2O.$$

As double salts containing barium chloride are almost unknown, we decided to test for its existence in crystal form by means of the solubility method which has previously been described.[2] The experiments were carried out first at 25°. Mixtures of barium chloride and mercuric chloride were prepared in varying proportions and treated with enough water to dissolve them when hot, allowing a crystal mass to form on cooling containing both mercuric and barium chlorides. In case no double salt formed, the solubility of the mixtures would be the same in all experiments while the composition of the residue which crystallized could vary between pure barium chloride on the one hand and pure mercuric chloride on the other. The solubility of the mixtures would not be the same throughout the series in case a double salt formed.

The mixtures, after being prepared as above described, were rotated in a thermostat for several days, when a sample of the solution was drawn off in a pipette through a filter of glass wool and analyzed. The residues were then removed, dried as quickly as possible between filter-paper, and analyzed. The analysis of both solution and residue was carried out by precipitating the solution, containing hydrochloric acid, with hydrogen sulphide. Mercuric sulphide was filtered off on a Gooch crucible, dried at 100° to 120°, and weighed. Barium was determined in the filtrate as sulphate. Water was calculated by difference. The following percentages were obtained at 25°:

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[1] Pogg. Ann., **17**, 130 (1829).

[2] This JOURNAL, **30**, 330, 339 (1903).

Table I.—Solubility of Mixtures of Barium and Mercuric Chlorides at 25°.

	$BaCl_2$ in solution.	$HgCl_2$ in solution.	$BaCl_2$ in residue.	$HgCl_2$ in residue.	H_2O in residue.
1	23.09	54.66	83.40	2.77	13.83
2	23.07	54.91	39.34	54.22	6.44
3	22.69	55.00	17.72	79.35	2.93
4	23.26	54.75	12.87	84.97	2.16
5	23.00	54.85	4.84	94.49	0.67

It will be noticed that the composition of the solutions remains practically constant throughout the series, while the residues vary between extreme limits, showing that *no double salt crystallizes at 25°.*

The solubility of each salt in water is largely increased by the presence of the other, indicating the formation of a complex salt in solution. It was therefore thought possible that a double salt might form at another temperature. Bonsdorf mentions that he obtained his double salt in the cold. To determine whether a double salt formed at some other temperature, a dilatometer was filled with a mixture of barium and mercuric chlorides moistened with the saturated solution of the salts, and with toluene to fill the air spaces and register the change in volume. A decided change in volume was observed between 17° and 18°, indicating a change in the solid phase. This was afterwards shown to be due to a double salt.

The dilatometer readings with the corresponding temperatures are given in Table II.

The dilatometer was cooled and warmed alternately to allow a mixture of the double salts and single salts to form. Placed again in a bath at 17°.6 the column gradually rose from 14.3 mm. to 14.9 mm. At 17° the column fell from 11.4 to 8.2 mm. The transition temperature would therefore be about 17°.2. The results in Table II. are shown graphically in Fig. I. The temperature is plotted as abscissa and the dilatometer readings as ordinate.

Table II.

Temperature.	Height of toluene in mm.
—3°.4	0.8
—1°.4	1.2
+1°.6	1.95
2°.6	2.45
5°.6	3.6
14°.6	6.1
16°.5	6.8
16°.7	6.9
17°.4	7.9
17°.6	11.8
18°.6	14.4
25°.6	18.3

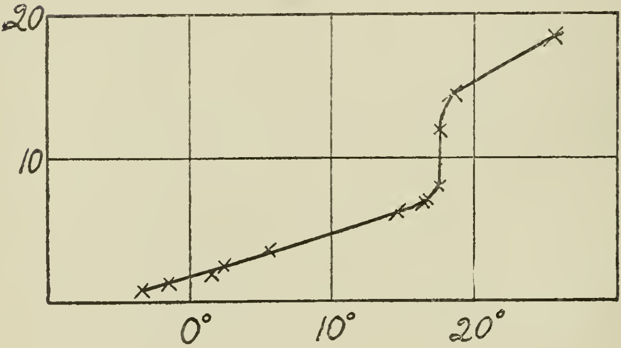

Fig. I.

To determine what change takes place at and below 17°.2, as indicated by the dilatometer, the solubility of mixtures of the two salts was determined at 10°.4. A constant temperature was obtained by means of the low-temperature thermostat described by one of us.[1] As the double salt which forms at this temperature was but a few degrees below its transition temperature where it breaks down into mercuric chloride and barium chloride, it was to be expected that the limits of its solubility would be very narrow, and this was found to be the case. It was prepared pure only after some trouble though mixtures of it with barium chloride or mercuric chloride were readily obtained. If solutions were prepared which were much supersaturated at 10°, only mixtures could be obtained of the double salt with one of the single salts, due to the fact that the single salts are not present in the same proportion in both solution and solid. On the other hand, if solutions were prepared which were but slightly supersaturated no salt would crystallize on shaking. The method adopted to obtain the pure double salt was to prepare solutions slightly supersaturated at the temperature of the experiment. To these solutions a minute quantity of crystals of the double salt and a single salt was added to start the crystallization. These crystals were obtained from a solution which was so much supersaturated that it would crystallize of itself. In this way pure double salt could be obtained which was proved by the fact that the composition of the solutions yielding the double salt varied somewhat while the composition of the residue remained practically constant.

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[1] Ztschr. phys. Chem., 33, 749 (1900).

The solubility results at 10°.4 are in Table III. In criticizing them, it must be remembered that the composition of the solution could be determined much more accurately than that of the residue, as the latter was contaminated with a certain amount of the mother-liquor containing a large proportion of dissolved salts.

In Nos 8 to 11 of the above table the pure double salt was present, as the solution varied, while the residue was nearly constant. The results on the composition of the residue are italicized in this case. They correspond closely to the salt $BaCl_2.3HgCl_2.6H_2O$, the calculated composition of which is added in the table.

That the salt decomposes at the temperature of a warm room was shown qualitatively by samples of the salt, which partly liquefied in tightly closed specimen-tubes. A salt with the formula given by Bonsdorf, $BaCl_2.2HgCl_2.2H_2O$, could not liquefy, as on decomposing the water, would be present in the right proportion to form crystallized barium chloride.

Table III.—Solubility of Mixtures of Barium and Mercuric Chlorides at 10°.4.

	$BaCl_2$ in solution. Per cent.	$HgCl_2$ in solution. Per cent.	$BaCl_2$ in residue. Per cent.	$HgCl_2$ in residue. Per cent.	H_2O in residue. Per cent.
1	23.55	50.54	66.94	21.27	11.79
2	23.48	50.59	49.25	38.00	12.75
3	23.69	50.55	28.80	59.55	11.65
4	23.62	50.41	22.50	66.47	11.03
5	23.52	50.65	21.41	67.50	11.09
6	23.57	50.56	19.56	69.90	10.54
7	23.64	50.51	19.36	70.06	10.58
8	23.44	50.74	*18.75*	*70.80*	*10.45*
9	22.58	51.23	*18.82*	*72.08*	*9.10*
10	22.48	51.41	*18.96*	*70.71*	*10.33*
11	22.10	51.66	*18.88*	*71.87*	*9.25*
	(Calculated for $BaCl_2.3HgCl_2.6H_2O$)		18.45	71.98	9.57
12	21.69	52.01	15.13	79.87	5.00
13	21.55	51.69	3.21	95.55	1.24
14	21.68	52.11	0.78	99.27	....

The solubility results at 25° and 10°.4 are shown in Fig. II.

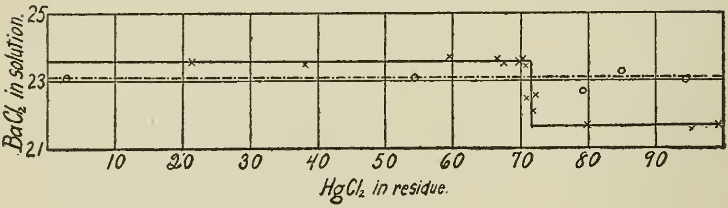

Fig. II.

The percentage of mercuric chloride in the residue is plotted as abscissa and the percentage of barium chloride in the solution as ordinate. The dotted horizontal line represents the solubility at 25°, where no double salt formed, and the other the solubilities at 10°.4.

Summary.

In the preceding article it has been shown :

1. That barium and mercuric chlorides do not form a double salt at 25°.

2. That a transition temperature exists at about 17°.2, below which the salt $BaCl_2.3HgCl_2.6H_2O$ forms.

3. That the salt $BaCl_2.2HgCl_2.2H_2O$, described by Bonsdorf does not form under the conditions which he gives. The solubility method, previously described, has been used to detect the presence of the double salt.

New Haven, Conn., March, 1904.

Contributions from the Sheffield Laboratory of Yale University.

ON THE SOLUBILITY OF POTASSIUM AND BARIUM NITRATES AND CHLORIDES.

By H. W. Foote.

The double nitrate of potassium and barium,

$$2KNO_3.Ba(NO_3)_2,$$

was described recently by Wallbridge.[1] As this salt was very unexpected, its solubility relations have been determined at 25° by the solubility method previously given. The solutions obtained were analyzed by evaporating them to dryness and weighing the residue after very gentle ignition. The residue was dissolved in water and barium determined as sulphate, after which potassium nitrate could be calculated. The composition of the residue was usually calculated, as water was absent. This could be done with sufficient accuracy by starting with known amounts of the two single salts and water. In one or two cases barium was determined as a check on this value.

The results obtained are in Table I., columns II. and III., showing the parts of potassium nitrate and barium nitrate, respectively, in 100 parts of solution. Where the pure double salt is present, the composition of the residue remains practically constant, while the solution varies. These results are italicized. In the other results, where a mixture was present either of potassium nitrate and the double salt (Nos. 6 to 9) or of the double salt and barium nitrate (Nos. 1 to 3) the composition of the residue varies while the solubility remains constant.

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[1] This Journal, 30, 154 (1903).

Table I.—Solubility of Potassium and Barium Nitrates at 25°.

I.	II. KNO_3 in solution.	III. $Ba(NO_3)_2$ in solution.	IV. KNO_3 in residue.	V. Residue contains:
1	15.24	6.64	5.14	$Ba(NO_3)_2$ and $2KNO_3.Ba(NO_3)_2$
2	14.69	6.60	26.76	“ “ “
3	14.79	6.62	38.66	“ “ “
4	*16.30*	*5.49*	*43.45*	$2KNO_3.Ba(NO_3)_2$
5	*21.99*	*3.04*	*43.25*	“
				(Calculated percentage of KNO_3 = 43.65)
6	27.66	2.01	50.52	KNO_3 and $2KNO_3.Ba(NO_3)_2$
7	27.81	2.09	64.10	“ “ “
8	27.94	1.92	81.27	“ “ “
9	27.64	2.05	93.45	“ “ “

The results in the table are represented graphically in Fig. I. The percentages of potassium nitrate in solution and in the residue are plotted respectively as ordinate and abscissa.

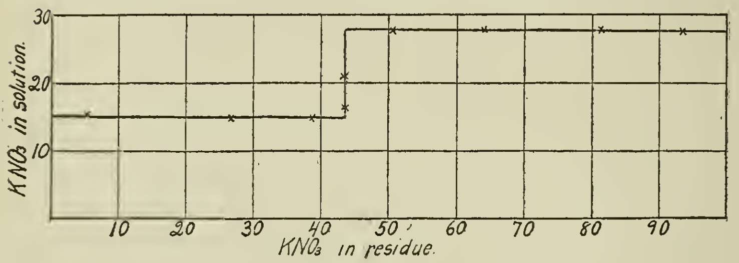

Fig. I.

The results show that the double salt can form at 25° under a moderately wide range of conditions, that is, it can form from solutions containing approximately from 15 to 27 per cent of potassium nitrate and from 6 to 2 per cent of barium nitrate.

The salt cannot be recrystallized, but would deposit at first crystals of barium nitrate if evaporated at 25°. This is shown by the fact that the solution of the double salt would contain a greater percentage of barium nitrate than of potassium nitrate, while all the solutions obtained above, including those in equilibrium with barium nitrate and the double salt, contain an excess of potassium nitrate.

A double salt of potassium and barium chlorides has never been prepared, and the solubility results given below in Table II. show that none forms at 25°.

Table II.—Solubility of Potassium and Barium Chlorides at 25°.

	KCl in solution. Per cent.	$BaCl_2$ in solution. Per cent.	KCl in residue. Per cent.
1	18.97	13.86	9.64
2	18.96	13.85	98.37

Had a double salt formed the solubility in the first experiment where a large excess of barium chloride was present would be different from the solubility in the second experiment, where the residue was nearly pure potassium chloride.

From results obtained by Rüdorf[1] on the solubility of mixtures of salts, it is very probable that ammonium chloride and sodium chloride also form no double salts with barium chloride.

New Haven, Conn., March, 1904.

ON SOME CUPRAMMONIUM SULPHATES.

By David W. Horn and Edytha E. Taylor.

The extensive investigations recently carried out on solutions of cuprammonium salts have made it desirable that the salts themselves be isolated and studied. This paper deals mostly with the cuprammonium sulphate longest known among the metal-ammonium compounds,

$$CuSO_4 + 4NH_3 + H_2O,$$

and the decomposition-products that have been given the formulas

$$CuSO_4 + 2NH_3 \quad \text{and} \quad CuSO_4 + NH_3.$$

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[1] Pogg. Ann., **148**, 467; Berliner Akad. Ber., 1885, 355.

Of these formulas, $CuSO_4 + 4NH_3 + H_2O$ has rested upon one analysis made by Berzelius[1] of apparently the same salt to which Bouzat has but recently[2] assigned a different formula—

$$CuSO_4 + 4NH_3 + 3/2H_2O.$$

The formulas $CuSO_4 + 2NH_3$ and $CuSO_4 + NH_3$ have had no basis in fact except the losses in weight observed by Kane[3] when the salt stated by Berzelius to be

$$CuSO_4 + 4NH_3 + H_2O$$

is heated at different temperatures. Changes in weight cannot be relied upon to differentiate ammonia having a molecular weight of 17 from water having a molecular weight of 18, even when the original substance is known to have a definite composition. For these reasons we proposed to prepare these substances, insuring the reliability of our preparations by complete analyses. Such analyses involve the difficulty of determining ammonia and water in a mixture of the vapors of the two, as well as that of determining sulphuric acid in copper compounds. We worked out reliable analytical methods and then studied the preparation and properties of the salt

$$CuSO_4 + 4NH_3 + H_2O,$$

its behavior at elevated temperatures, and the properties of its aqueous solution. This paper presents these points in order.

I. Analytical Methods.

(*A*) *Determination of Copper.*—We first tried a rapid electrolytic method proposed by Wagner[4] for the determination of copper. The deposits were not uniform, but contained here and there brownish lumps. When the electrolysis was pushed so far that hydrogen sulphide no longer gave a precipitate in the liquid that was being electrolyzed, the results were high. This is illustrated by the following analysis:

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[1] Gilbert's Ann., **40**, 300.

[2] Ann. chim. phys., [7], **29**, 305 (1903).

[3] *Ibid.*, [2], **72**, 265.

[4] Ztschr. Elektrotech. u. Elektrochem., **2**, 613–616.

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1.0081	0.2621	25.99	25.86

We then adopted Rose's method[1] of heating the dehydrated sulphates with sulphur in an atmosphere of hydrogen. The following analyses are given to show the degree of accuracy of the method:

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.5419	0.1401	25.87	25.86
0.4059	0.1049	25.87	
0.7004	0.1812	25.87	
0.5650	0.1463	25.89	
0.3632	0.0939	25.86	
0.5382	0.1392	25.87	
0.2811	0.0726	25.83	
0.4356	0.1126	25.86	
0.3921	0.1014	25.89	
0.4914	0.1271	25.84	
0.3146	0.0813	25.84	
0.3710	0.0960	25.87	

(*B*) *Determination of Ammonia.*—The usual method of distillation with an alkali was used. When the alkali was previously treated with potassium permanganate the results were invariably low in the case of copper compounds, although when ammonium borate was used to test the method the results were good. We used sodium hydroxide free from nitrogen. Lime was added to the alkaline liquids to prevent "bumping" during the distillations. It was found that the ammonia could only be completely removed from the copper compounds when the distillations were continued until the residues in the distilling-flasks reached approximately the concentration of 1 gram sodium hydroxide in 1 cc. to 1.5 cc. of the liquid. In order to prevent the mechanical carrying-over of alkali in the distillations we found it advisable to use long-necked balloon-flasks of about 2.5 liters capacity, and to distil at such a rate that the condenser-tube was but one-fourth to one-third full of uncondensed water-vapor. To avoid loss of ammonia the salts were weighed into a slight excess of acid contained in the distilling-flasks. The following analyses of the salt $CuSO_4 + 4NH_3 + H_2O$ show to what extent the method can be relied upon when the precautions mentioned are taken :

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[1] Anal. Chem., II., 173-4 (sixth German edition.)

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.3521	0.0980	27.82	27.76
0.3969	0.1099	27.70	
0.2974	0.0825	27.76	
0.5006	0.1393	27.82	
0.3806	0.1057	27.77	
0.3049	0.0844	27.71	
0.4766	0.1322	27.74	

As already mentioned, ammonium borate may be used advantageously in testing the apparatus in the distillations, because the ammonia in it can be determined by direct titration as well as by distillation.

(*C*) *Determination of Water and Ammonia.*—Water and ammonia are evolved simultaneously by the salt $CuSO_4 + 4NH_3 + H_2O$ when it is heated. We determined them by heating a weighed quantity of the salt in a boat in a tube so arranged that a current of air, dry and free from carbon dioxide, could pass over the heated material and carry the water and ammonia evolved into absorption apparatus. We used air that had been passed through dilute sulphuric acid and barium hydroxide solutions, and then over solid sodium hydroxide and potassium hydroxide. The air leaving this apparatus entered the tube containing the boat through a piece of ordinary glass tubing about 2 meters long. The end of this connecting tube nearest the boat was drawn to a capillary tip in order to prevent as far as possible the diffusion of the ammonia backward toward the apparatus for purifying the air. The larger tube, in which the boat was heated, was placed in a cylindrical air-bath of about four times the length of the boat. This tube was joined directly to the absorption-apparatus consisting of two glass-stoppered U-tubes filled with solid potassium hydroxide to absorb the water evolved, and a similar tube containing glass beads and 65 per cent sulphuric acid (to absorb the ammonia) joined with two more tubes of potassium hydroxide to absorb the water given off by the acid. We tested this apparatus and method for the determination of water using crystallized barium chloride, the loss in weight of the boat checking on the changes in weight in the absorption-tubes. There was no occasion to test the absorption of ammonia by the acid. The results of eight analyses made by this method are given below, on pages 272 and 273.

The current of air used in these and other similar experiments was furnished by a simple apparatus that has since been found so useful in the laboratory that it will be described. A Bunsen pump passing through a rubber stopper is fitted into the middle opening of a Wolff bottle; into one of the side openings a siphon-tube is fitted by a rubber stopper, the arm of the tube within the bottle reaching almost to the bottom of the bottle; into the other opening there is fitted a tube bent at a right angle and cut off just beneath the rubber stopper through which it passes. The pump supplies water and air, the former being drawn off or forced out through the siphon-tube and the latter being drawn as needed from the other (outlet) tube. In using this apparatus the only precaution to be observed is that neither water nor air be drawn off faster than it is supplied by the pump. If the outlet of the siphon-tube be small, the air is supplied under considerable pressure.

(*D*) *Determination of Sulphuric Acid.*—Precipitated barium sulphate "carries down" copper salts[1] perhaps more freely than it does iron salts. For this reason it is imperative that the copper and sulphuric acid be separated quantitatively, leaving the latter under such conditions that it can be precipitated as (relatively) pure barium sulphate.

It is apparent that in this case the copper cannot be precipitated as sulphide. Gibbs proposed[2] to precipitate copper with sodium carbonate. We precipitated copper by this method as directed in Fresenius' "Quantitative Analysis,"[1] after we had treated the salt with a slight excess of dilute hydrochloric acid. The following were the results obtained by the careful precipitation of barium sulphate in the filtrates from the copper precipitates after an excess of hydrochloric acid had been added to these filtrates :

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[1] Berzelius: Ann. chim. phys., [2], 14, 376.

[2] Ztschr. anal. Chem., 7, 258.

Weight of salt taken for analysis. Gram.	Weight of SO_4 found. Gram.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.2832	0.0825	29.12	39.06
0.3666	0.1076	29.36	
0.2522	0.0763	30.25	
0.3754	0.1108	29.52	

These figures showed that the precipitates contained sulphuric acid which had been retained although the precipitates had been washed till the wash-waters no longer reacted with barium chloride. The presence of sulphuric acid in similar precipitates was proven later by qualitative tests, which also showed that the precipitates consisted partly of carbonates. The four original precipitates were analyzed for copper by Rose's method. The results showed the completeness of the previous precipitations of copper, and that the precipitates could be washed free from alkali salts ; they also served along with the sulphuric acid determinations already given to show that the proportion of copper to sulphuric acid in the (Gibbs) precipitates is very approximately 4 : 1.

Number of precipitate taken.	Weight of copper found. Gram.	Percentage of copper found in salt.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.0733	25.87	25.86
2	0.0952	25.97	
3	0.0654	25.93	
4	0.0971	25.87	

The advantages of Gibbs' method for precipitating copper are sufficiently clear. However, it cannot be used to separate sulphuric acid from copper because the green precipitate contains one equivalent of sulphuric acid to every four of copper present.

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[1] Sixth German edition, I., 331.

The copper was next precipitated as hydroxide by the addition of caustic potash to solutions of the salt (previously made slightly acid with hydrochloric acid), according to the directions of Fresenius.[1] The precipitates were difficult to wash and when tested qualitatively were always found to contain sulphuric acid, although the wash-waters from them had no longer reacted with barium chloride. The following analyses (1–4) of the precipitates for copper by Rose's method show that they had probably retained alkali salts in addition to the sulphuric acid already mentioned; analyses 5 and 6 were made by applying Rose's method to the original salt and are given for comparison:

Number of analysis.	Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.3474	0.0913	26.23	25.86
2	0.4444	0.1168	26.28	
3	0.6471	0.1690	26.11	
4	0.5107	0.1337	26.17	
5	0.3146	0.0813	25.84	
6	0.3546	0.0916	25.85	

We next tried adding the solution of the copper salt, previously acidified with hydrochloric acid, to an excess of caustic soda. The precipitates thus formed are comparatively easily washed, and afterward do not contain any sulphuric acid. Further, in this procedure it is not necessary to use a large excess of alkali so that after the filtrates have been acidified and before the sulphuric acid in them is precipitated they contain comparatively small amounts of alkali salts. This is an advantage, because alkali salts are also "carried down" by barium sulphate. There is a further advantage in using caustic soda, for potassium salts are "carried down" in larger quantities than sodium salts.[2] The results given on page 267 show the degree of accuracy of this method. In detail, the procedure was as follows:

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[1] *Loc. cit.*, p. 329.

[2] Kretschy: Ztschr. anal. Chem., **10**, 396.

A quantity of the copper salt containing about 0.09 gram of copper was weighed into a small beaker containing about 50 cc. of water. Hydrochloric acid was then added until the precipitate at first formed had completely redissolved. About 150 cc. of a solution of sodium hydroxide (free from sulphates), containing 2 grams of sodium hydroxide per liter, were heated to boiling in a large beaker. The copper solution was slowly stirred into the boiling liquid, the transfer being completed with water. The mixture was boiled gently for a few minutes and then digested for about half an hour just below the boiling temperature. The solution was filtered while hot. The precipitate, which had been retained in the beaker, was washed four times by decantation with hot water; it was then transferred to the filter and again washed with hot water until the wash-waters did not give a precipitate with barium chloride. The precipitate was then tested for sulphuric acid after it had been dissolved in dilute hydrochloric acid. The entire filtrate was acidified with hydrochloric acid and treated with an excess of barium chloride, observing the well-known precautions. The barium sulphate was treated as is usual.

The suggestion of Küster and Thiel to "remove the ion"[1] that interferes in precipitations of barium sulphate was tried in each of the above cases. The following are the records of the experiments:

I. Copper was precipitated by sodium carbonate, an excess of barium chloride was added to the hot mixture, and then an excess of hydrochloric acid was added to dissolve the copper precipitate. The barium sulphate was digested with the acid solution about half an hour, and then collected and treated as usual. The results are among those given below and are numbered 1 and 2.

II. Copper was precipitated by adding caustic potash; the rest of the treatment was as in I. The results are numbered 3 and 4.

III. Copper was precipitated by adding the solution containing it to an excess of caustic soda; the rest of the treatment was as in I. The results are numbered 5 and 6.

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[1] Ztschr. anorg. Chem., 19, 99.

Number of analysis.	Weight of salt taken for analysis. Gram.	Weight of SO_4 found. Gram.	Percentage of SO_4 found.	Percentage of SO_4 calculated for $CuSO_4 + 4NH_3 + H_2O$.
1	0.2611	0.1068	40.91	39.06
2	0.2548	0.1047	41.11	
3	0.2642	0.1052	39.83	
4	0.2757	0.1087	39.44	
5	0.2135	0.0847	39.67	
6	0.2088	0.0832	39.84	

In our opinion the method of Küster and Thiel is not applicable in the presence of copper.

II. Preparation of the Salt $CuSO_4 + 4NH_3 + H_2O$.

(*A*) *Berzelius' Method.*—The preparation of this salt is said to have been described first by Stisser.[1] Berzelius, however, was the first to assign a formula to it. The method of preparation advised by him consists in treating a solution of copper sulphate with an excess of ammonia water and adding alcohol to the resulting purple solution. If the alcohol be carefully poured upon the purple solution, crystals of the salt form at the surface of contact of the two liquids. If the alcohol be slowly added and mixed with the purple solution, the salt separates as a pulverulent crystalline deposit.

We have found that in any case the salt is very unstable after it is removed from its mother-liquor. Only small quantities of it can be dried between filter-papers or on unglazed porcelain plates without considerable decomposition. This decomposition is clearly indicated by the odor of ammonia above the salt. The following are analyses of small quantities of the salt dried thus as quickly as possible:

	Weight of salt taken for analysis. Grams.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
I.	1.1978	0.3296	27.51 (T)[2]	27.75
II.	0.6519	0.1797	27.57 (T)[2]	

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[1] 1693. See Roscoe and Schorlemmer, II., 1, 339.

[2] All experiments and analyses made by E. E. Taylor will be marked (T).

If larger quantities are dried, even though they are first washed with absolute alcohol, the decomposition has time to go much further, as is seen from the following analyses of a specimen of perhaps 30 grams:

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.4979	0.1298	26.07(T)	27.75
0.5022	0.1326	26.50(T)	
0.4852	0.1245	25.66(T)	

If the salt is prepared in large crystals, as it readily can be, and the surfaces of these are quickly dried with filter-paper, a pure product is not obtained because the mother-liquor is occluded in large amounts by the crystals.

Bouzat prepared crystals of this salt for use in his calorimetric studies, by cooling a hot concentrated solution of it and quickly drying the crystals that separated between filter-paper. His methods of analysis are not described in his paper, but the analyses for ammonia of his preparation gave results surprisingly like those we obtained by analyzing the same salt dried in the same way, but known by us to have partly decomposed in the drying. He found for ammonia, 26.25 and 26.45 per cent.[1] He ascribes to the salt the formula $CuSO_4 + 4NH_3 + 3/2H_2O$, which represents a salt containing 26.77 per cent ammonia.

The analysis given by Berzelius is as follows:

	Calculated for $CuSO_4 + 4NH_3 + H_2O$.	Found.
CuO	32.37	32.22
SO_3	32.55	32.58
NH_3	27.75	27.89
H_2O	7.33	7.31
	100.00	100.00

Though the pure salt cannot be prepared by drying between filter-papers, apparently it can be prepared in some other way.

We prepared a quantity of the salt by Berzelius' method and quickly transferred specimens of it from its mother-liquor to unglazed porcelain plates, in desiccators. The desiccators contained, respectively, calcium chloride, sulphuric acid, solid potassium hydroxide, and a small vessel of strongest ammonia water, and lime. In the first and second desiccators the salt soon became opaque in spots on its surface. In the third, the crystals seemed to change only in color, though it was found later that they were losing weight slowly at the same time. In the fourth desiccator (over lime), no change in the salt could be seen.

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[1] *Loc. cit.*, p. 356.

The steady loss in weight of the crystals over potassium hydroxide and ammonia water was observed for two weeks. Several of the crystals were then analyzed for ammonia with the following results :

Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.4989	0.1395	27.97(T)	27.75
0.4895	0.1372	28.03(T)	

Under these conditions the salt had apparently taken up more ammonia. We have studied this change in the salt further and will refer to it later (p. 268). Kohlschütter has since[1] used this same method for drying the cuprammonium salts used in his investigations. Reference to his paper will show that his analytical results for ammonia are also high.

The crystals dried over lime soon ceased to change in weight. Some of the salt thus dried was finely ground and put in a vacuum over lime ; it was weighed at intervals with the following results :

	Gram.
Original weight	0.6736
Weight after 13 hours	0.6733
Weight after 40 hours	0.6733

We then prepared more of the salt by Berzelius' method, precipitating it as a crystalline powder. This was dried over lime and analyzed for copper and ammonia with the following results :

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[1] Ber. d. chem. Ges., **37**, 1153-70 (1904).

	Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
I. Cu	0.6918	0.1785	25.80(T)	25.86
	0.4882	0.1573	25.73(T)	
	0.4888	0.1581	25.84(T)	

	Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
II. NH_3	0.3098	0.0860	27.76(T)	27.75
	0.4184	0.1161	27.75(T)	
	0.4184	0.1157	27.65(T)	

These analyses of the purple cuprammonium sulphate are in accord with that by Berzelius, upon which the formula $CuSO_4 + 4NH_3 + H_2O$ is based.

(*B*) *Mallaert's Method.*—The method suggested by Mallaert[1] for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$ consists in the action of ammonia gas on solid $CuSO_4 + 5H_2O$. We observed a very rapid change to purple color when finely ground copper sulphate was put in a desiccator over ammonia water. This promised to be a convenient method for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$, provided the purple product is of this composition.

"Pure" copper sulphate was recrystallized five times from water and its purity assured by the following analyses of the (air-dried) product:

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 5H_2O$.
0.4404	0.1121	25.47	25.47
0.4267	0.1087	25.47	
0.3598	0.0915	25.44	

Specimens of this salt were weighed into porcelain boats and the boats put into glass tubes in a current of air that had first bubbled through ammonia water (sp. gr. 0.09). The boats were frequently transferred rapidly to well-ground glass-stoppered weighing-tubes and weighed. The following were the results:

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[1] Jour. de Pharm. d'Anvers, 1848, 217; Jsb. (Svanberg), **30**, 119 (1851).

Time in minutes.	Weight of specimen. I.	Weight of specimen. II.	Changes in weight. I.	Changes in weight. II.
	Grams.	Grams.	Gram.	Gram.
0	2.0622	1.5436		
15	2.3575	1.8485	+0.2953	+0.3049
40	2.4628	1.8994	+0.1053	+0.0509
55		1.9035		+0.0041
60	2.5170		+0.0442	
85	2.5261	1.8912	+0.0991	—0.0123
105	2.5238		—0.0023	
135	2.4911(T)		—0.0327	
150		1.8608(T)		—0.0304

The weighings were continued for half a day longer and showed continued losses. At the end of that time the specimens were about 0.3 gram heavier than the original $CuSO_4 + 5H_2O$. The above figures show maxima corresponding to gains in weight of 22.5 and 23.2 per cent, respectively. A gain of 24 per cent would represent the addition of 3 molecules of ammonia to each molecule of $CuSO_4 + 5H_2O$. Such addition-products have been described, especially in connection with the action of hydrochloric acid on copper sulphate;[1] for example, $CuSO_4 + 5H_2O + 3HCl$.

Whatever may be the case in other instances, the products here are mixtures, as was clearly shown by the mixed colors of the contents of the boats after drying over lime. The colors ranged from sky-blue to purple. The action by which the colored mixtures are produced is accompanied by considerable evolution of heat.

To avoid the mechanical retention of much water on the surface of the salt (as was the case in the glazed porcelain boats), and to allow sufficient time for the action to complete itself, pure copper sulphate was next placed on an unglazed porcelain plate in a desiccator containing ammonia water (sp. gr. 0.9). The following analyses for ammonia were made of specimens that were dried over lime after removal from the desiccator containing ammonia water. I. was a specimen taken after three days, and II. was a specimen taken after four months:

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[1] Latschinoff: J. Russ. Phys. Chem. Soc., 1888, pp. 586, 657, 707. Jsb., 1, 621 (1888); 1, 517 (1889).

	Weight of salt taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 4NH_3 + H_2O$.
I.	0.3577	0.0962	26.93	27.75
II.	0.4305	0.1191	27.70	
	0.4594	0.1278	27.82	

From the analyses of II. it might be inferred that the final product of the action of ammonia gas on pentahydrated copper sulphate is $CuSO_4 + 4NH_3 + H_2O$, as was stated by Mallaert. This was disproved in two ways; first, by the analyses of II. for copper, and second, by the fact that II. was not completely soluble in water but left a green insoluble residue. The analyses for copper resulted as follows:

Weight of salt taken for analysis. Gram.	Weight of copper found. Gram.	Percentage of copper found.	Percentage of copper calculated for $CuSO_4 + 4NH_3 + H_2O$.
0.2945	0.0769	26.13	25.87
0.3227	0.0843	26.13	

We conclude that the product of the action of ammonia gas on pentahydrated copper sulphate is not the salt

$$CuSO_4 + 4NH_3 + H_2O,$$

as stated by Mallaert, and as indicated by the percentage of ammonia found in the final product, but that it is a mixture containing basic salts or copper oxide.

(*C*) *Andrae's Method.*—Andrae[1] has stated that when ammonia gas is passed into a solution of copper sulphate fine crystals of the salt $CuSO_4 + 4NH_3 + H_2O$ separate out as the concentration of ammonia in the liquid rises. Analyses are not given in Andrae's paper. This method by which the solid is produced gradually and in fine crystals is, in our opinion, the best for the preparation of the pure salt.

We prepared several hundred grams of the salt by this method and dried it over lime. We then made a complete analysis of it, and have used it as the basis for the rest of our work. The following results were obtained in its analysis:

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[1] Compt. rend., 100, 1138.

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 4NH_3 + H_2O$.
Cu	0.3543	0.0916	25.86	25.86
	0.4790	0.1239	25.87	
	0.5120	0.1325	25.88	
	0.4907	0.1268	25.84	
SO_4	0.3378	0.1324	39.19(T)[1]	39.06
	0.2631	0.1026	39.00(T)	
	0.3100	0.1212	39.09(T)	
	0.3383	0.1322	39.08(T)	
NH_3	0.4419	0.1220	27.61(T)	27.75
	0.3927	0.1092	27.80(T)	
	0.5358	0.1488	27.77(T)	
	0.3833	0.1067	27.84(T)	
H_2O	0.6691	0.0494	7.38[2]	7.33
	0.5701	0.0417	7.31	
	1.2860	0.0944	7.34	
	0.5967	0.0438	7.34	

Specimens taken from this quantity of salt were used in all of the subsequent experiments involving $CuSO_4 + 4NH_3 + H_2O$ described in this paper.

III. Properties of the Salt $CuSO_4 + 4NH_3 + H_2O$.

The dry salt is odorless. However, ammonia is given off by it instantly when it is moistened, and very soon when it is exposed to the air. It is perfectly stable when kept in a closed space over lime, as is proven by the following analyses of a specimen taken from that quantity, the complete analysis of which has just been given. This specimen had been kept over lime one year:

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 4NH_3 + H_2O$.
Cu	0.4102	0.1060	25.85	25.86
	0.5012	0.1297	25.87	
	0.5209	0.1348	25.88	
NH_3	0.4766	0.1322	27.74	27.75
	0.5006	0.1393	27.82	
	0.3806	0.1057	27.77	

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[1] Determined by method described on page 260.

[2] Determined by method described on page 256.

The dry salt is not stable in a vacuum over concentrated sulphuric acid, as is shown by the following weighings of a finely ground specimen of it that was treated in this way :

	Gram.
Original weight	0.4371
Weight after twenty-four hours	0.4355
" " fifty-two "	0.4328
" " three hundred and sixteen hours	0.4144

The salt dissolves readily in small quantities of water, giving perfectly clear solutions. Its solubility in water between 21° and 22° C. was determined by sealing a quantity of the salt in a glass tube with a quantity of water that was not sufficient to dissolve it, and shaking the tube four hours. The contents of the tube were centrifuged after the shaking was complete and before the tube was opened. Two weighed quantities of the clear liquid then taken from above the crystals in the tube, by means of a pipette, were evaporated to dryness and analyzed for copper. The results were as follows :

Weight of solution analyzed. Grams.	Weight of Cu_2S found. Gram.	Weight of Cu_2S yielded by 1 gram of solution.
2.2723	0.2252	0.0991
1.4955	0.1481	0.0990

The corresponding weight of the salt $CuSO_4 + 4NH_3 + H_2O$ that was dissolved by 100 grams of water at 21° to 22° C. was 18.05 grams.

The salt takes up ammonia in a desiccator over sticks of potassium hydroxide and a very little ammonia water. This has been proven already on page 263. In this first experiment, however, the analyses were made after the salt had been exposed thus for only about two weeks. Latschinoff has stated that the molecule of water in the salt $CuSO_4 + 4NH_3 + H_2O$ is replaced by a molecule of ammonia, in an atmosphere of dry ammonia. In another experiment, therefore, we kept this salt over sticks of potassium hydroxide and a few drops of concentrated ammonia water for four months before the following analyses of the resulting product were made :

Constituent determined.	Weight of salt taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 5NH_3$.
NH_3	0.4513	0.1558	34.52	34.83
	0.3517	0.1217	34.59	
Cu	0.3638	0.0946	26.01	25.97
	0.4145	0.1079	26.02	

The salt had not lost its crystalline form in the four months. Its color had become less purple (bluer) than it was originally.

The analyses show that under the stated conditions ammonia had entered the molecule of the salt in the place of water; they show in addition to this, however, that the reaction is not a clean one, resulting in the formation of the compound $CuSO_4 + 5NH_3$, but one giving rise to mixed products containing basic salts or copper oxide.

IV. Behavior of the Salt $CuSO_4 + 4NH_3 + H_2O$ at Elevated Temperatures.

Kane has stated that when the salt $CuSO_4 + 4NH_3 + H_2O$ is heated at a temperature not above 149° C. it loses one-half of its ammonia and all of its water, and that the residue is an "apple-green powder" of the composition $CuSO_4 + 2NH_3$; that at temperatures not above 203° C. one-half of the remaining ammonia is lost, giving a residue of the composition $CuSO_4 + NH_3$; and that at 260° C. all of the ammonia is driven off and anhydrous copper sulphate remains.

In Kane's memoir there are the results of only three experiments upon this subject, and these we tabulate :

Weight of salt heated. Grams.	Weight of residue. Grams.	"Parts in 100" of residue.	Percentage loss in weight by heating.	Percentage loss calculated if $CuSO_4 + 2NH_3$ is residue.
1.969	1.545	78.47	21.53	21.20
4.921	3.854	78.32	21.68	
5.042	3.921	77.77	22.23	

In this connection Kane says : "The calculated percentage composition of ammoniacal copper sulphate is :

SO_3	32.58
CuO	32.22
$2NH_3$	27.89
HO	7.31
	100.00

which is evidently transformed by heat into

$CuO.SO_3$	64.80	HO	7.31
NH_3	13.95	NH_3	13.94
	78.75		21.25

Thus it is demonstrated by experiment that by the first action of heat all of the water and half of the ammonia is driven off, and that the green residue consists of copper sulphate united with one equivalent of ammonia. * * * I have tried to separate the water without loss of ammonia by the most careful management of the flame, but could not."

It is surprising that there is in the memoir no other evidence than this of the formation and composition of what are announced by Kane to be new compounds. As has already been pointed out, losses in weight cannot be relied upon to differentiate water from ammonia. Thus, if three-fourths of the ammonia had separated from the salt at 149° C., instead of half of it and all of the water, the loss in weight would have been 20.81 per cent instead of 21.20 per cent. It is true that Kane proved in some way, to his own satisfaction, that water is given off with the ammonia, but how he determined that *all* of the water is given off it is impossible to say. We shall show later that the same salt as that with which he was working when heated to 100° C. instead of 149° C. loses on the average 21.12 per cent. This percentage loss differs less from the 21.20 per cent that was his standard of reference than do his own experimental results, yet at 100° C. the salt (we shall show) loses more than half of its ammonia and probably retains a little of its water.

In discussing the change in the salt $CuSO_4 + 4NH_3 + H_2O$

at 203° C., Kane gives no figures and no description of the product.

(*A*) *Behavior of the Salt $CuSO_4 + 4NH_3 + H_2O$ at 149° C.*—We fitted out a copper air-bath with a Reichert gas-regulator so that the temperature in the bath could not rise above 149° C. We heated a specimen of the pure $CuSO_4 + 4NH_3 + H_2O$ in this bath for two hours. The product was an "apple-green powder." The following results were obtained when this product was analyzed for ammonia:

Weight of powder taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 2NH_3$.
0.6815	0.1130	16.58(T)	17.61
0.6522	0.1080	16.56(T)	
0.6516	0.1076	16.51(T)	

Another quantity of the pure salt $CuSO_4 + 4NH_3 + H_2O$ was then heated in a Victor Meyer bath containing a fraction of illuminating oil boiling between 144° and 147° C. After a few hours the product was removed and analyzed for ammonia and copper. It is interesting to note that the product was again of an "apple-green" color, and that it was of a different shade of green from that produced in the former experiment. The analytical results were as follows:

Constituent determined.	Weight of powder taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage calculated for $CuSO_4 + 2NH_3$.
NH_3	0.5085	0.0861	16.93(T)	17.61
	0.5087	0.0863	16.96(T)	
	0.4840	0.0822	16.98(T)	
Cu	0.4597	0.1513	32.92	32.82

The insufficiency of Kane's data is emphasized by these experiments. The "apple-green powders" were mixtures whose uniformity depended upon the fact that they were stirred thoroughly during the heatings. Their composition is not even approximately represented by the formula

$$CuSO_4 + 2NH_3.$$

No more direct way to find out just what takes place when the salt $CuSO_4 + 4NH_3 + H_2O$ is heated at 149° C. suggested itself than to heat weighed quantities of the pure salt under such conditions that all the water and ammonia evolved by it could be collected separately and weighed, and the residue weighed. The apparatus used for this purpose has been described on page 256. The results of four experiments, lasting two hours each, were as follows :

Weight of salt heated. Gram.	Weight of residue after heating. Gram.	Percentage loss in weight during heating.	Weight of water collected during heating. Gram.	Percent'ge weight lost by salt as water.	Weight of ammonia collected during heating. Gram.	Percent'ge weight lost by salt as ammonia.
0.6691	0.5255	21.46	0.0494	7.38	0.0953	14.24
0.5701	0.4481	21.39	0.0417	7.31	0.0807	14.15
0.5846	0.4597	21.37	0.0431	7.37	0.0828	14.16
0.5260	0.4135	21.39	0.0388	7.38	0.0745	14.16

Calculated percentage loss in weight when $CuSO_4 + 4NH_3 + H_2O$ is converted into $CuSO_4 + 2NH_3 = 21.20$.

Calculated percentage of water in the salt $CuSO_4 + 4NH_3 + H_2O = 7.33$.

One-half the calculated percentage of ammonia in the salt $CuSO_4 + 4NH_3 + H_2O = 13.8$.

Analyses of the residues for ammonia resulted as follows :

Weight of residue taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.	Percentage of ammonia calculated for $CuSO_4 + 2NH_3$.
0.2379	0.0417	17.48(T)	17.61
0.3182	0.0552	17.35(T)	

These experiments show that even when the salt $CuSO_4 + 4NH_3 + H_2O$ is decomposed in dry air at 149° C. the product is not a definite chemical compound but a mixture that approximates in composition to the formula $CuSO_4 + 2NH_3$. This mixed product has a pale-blue color, in no way like the "apple-green" color of the products in the previous experiments.

(*B*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 125° C.* —A recent paper by Sabbatani that was available to us only in abstract[1] states that at temperatures from 120° to 125° C. both of the salt $CuSO_4 + 4NH_3 + H_2O$ and $CuCl_2 + 4NH_3 + H_2O$ lose half of the ammonia and all of the water they contain. The abstract gives no details. We carried out experiments with specimens of the first of these two salts at 120° to 125° C. in the same apparatus as those at 149° C. The results were as follows:

Weight of salt heated. Grams.	Weight of residue after heating. Grams.	Percentage loss in weight during heating.	Weight of water collected during heating. Gram.	Percent'ge weight lost by salt as water.	Weight of ammonia collected during heating. Gram.	Percent'ge weight lost by salt as ammonia.
1.2860	1.0126	21.25	0.0944	7.35	0.1812	14.09
0.6195	0.4872	21.34	0.0465	7.50	0.0868	14.01
0.5967	0.4699	21.25	0.0438	7.35	0.0811	13.59
0.4099	0.3225	21.32	0.0297	7.25	0.0558	13.63

The percentage losses are less than at 149° C. and the product approaches in composition more nearly to the formula $CuSO_4 + 2NH_3$. The color differed very little from that of the product at 149° C., being slightly bluer.

(*C*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 100° C.*— We noticed that this salt is decomposed also at 100° C. When heated in dry air at 100° C. a product having constant weight is finally obtained. The following results show this, and, incidentally, the accuracy associated with all the experiments in this paper that involve the weighing of boats and residues:

		Grams.
(6)	Total weight (tube, boat, and residue)	10.39500
	Weight after twelve hours more at 100° C.	10.39358
	" " twenty " " " " "	10.39359
	" " thirty-six hours more at 100° C.	10.39351
(7)	Total weight (platinum boat and residue)	1.16791
	Weight after three hours more at 100° C	1.16791
(8)	Total weight (platinum boat and residue)	1.21362
	Weight after six hours more at 100° C.	1.21363

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[1] Jsb., **1**, 96 (1897); Ann. Chim. Pharm., **26**, 337.

Repeated experiment showed that the losses in weight are not always the same. This is readily seen from the following figures :

Number of experiment.	Weight of salt heated. Gram.	Weight of residue after heating. Gram.	Percentage loss in weight.
1	0.4894	0.3878	20.75(T)
2	0.4564	0.3606	20.99
3	0.4164	0.3273	21.39(T)
4	0.4664	0.3669	21.33
5	0.4332	0.3410	21.28(T)
6	0.4184	0.3300	21.24

The analyses of the products in these experiments indicated that they were of varying composition :

Constituent determined.	Weight of residue taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.
NH_3	0.8167	0.1358	16.62(T)
	0.2201	0.0368	16.72(T)
	0.1911	0.0324	16.83(T)
	0.2393	0.0394	16.48(T)
Cu	0.2311	0.0741	32.07
	0.1873	0.0602	32.18
	0.2215	0.0896	32.23

Latschinoff has stated that when hydrochloric acid is led over pentahydrated copper sulphate at room temperature there results by degrees the compound $CuSO_4 + 5H_2O + 3HCl$, and by further action the compound $CuSO_4 + 2H_2O + 2HCl$, which breaks down when air is led over it into $CuSO_4 + H_2O + \frac{1}{8}HCl$. This $\frac{1}{8}HCl$ cannot be removed by a stream of air. He has also stated that when the compound $CuSO_4 + 5NH_3$ is heated under certain conditions the final product is $CuSO_4 + \frac{1}{4}NH_3$. Evidence of this kind is of especial interest as bearing upon the molecular weight of (solid) copper sulphate. At first we believed that the residue we obtained at 100° C. might be classed with these interesting compounds. Thus, if the product was fairly represented by the formula $CuSO_4 + 1\frac{7}{8}NH_3 + \frac{1}{8}H_2O$ it would be formed from the salt $CuSO_4 + 4NH_3 + H_2O$ by a loss of 21.15 per cent, and it would contain 16.50 per cent ammonia and 32.79 per cent copper. The experimental results that have been given do not quite agree with these calculated values, but approximate to them. This might be due to the water evolved from some of the salt acting upon those, or other, parts of the specimen producing mixed products. To avoid this as far as possible we heated very small quantities of pure $CuSO_4 + 4NH_3 + H_2O$, carefully spread out in thin layers on the bottom of a thin platinum boat. This boat was used to distribute better the error in weighing. The following results were thus obtained :

Number of experiment.	Weight of salt heated. Gram.	Weight of residue after heating. Gram.	Percentage loss in weight.
7	0.0682	0.0537	21.21
8	0.1261	0.0996	20.96
9	0.1112	0.0877	21.08
10	0.1746.	0.1377	21.15
11	0.1617	0.1276	21.09
12	0.2644	0.2085	21.12

Several of the residues were analyzed :

Number of experiment.	Constituent determined.	Weight of residue taken for analysis. Gram.	Weight of constituent found. Gram.	Percentage of constituent found.	Percentage of constituent calculated for $CuSO_4 + 2NH_3$.
9	Cu	0.0870	0.0281	32.29	32.82
10		0.1373	0.0447	32.58	
11		0.1275	0.0418	32.76	
12	NH_3	0.2084	0.0365	17.49	17.61

These results are not in agreement with the formula we have tentatively assumed. If the product could be correctly represented by the formula $CuSO_4 + 1\frac{3}{4}NH_3 + \frac{1}{4}H_2O$, its formation should be preceded by a loss in weight of 21.12 per cent, whereas the average of these last six experiments is 21.10 per cent. But this formula requires 15.39 per cent ammonia.

It is not possible to find any one formula to fit all the data at hand. Whatever may be the case in other instances, our experiments leave no doubt that at 100° C. $CuSO_4 + 4NH_3 + H_2O$ yields a mixed residue.

We believe that the action of water is responsible for the production of these mixtures. We tested this by heating the salt $CuSO_4 + 4NH_3 + H_2O$ at 100° C. in a bath where the vapor of water had access by free diffusion to the heated material. The material in the bath was stirred frequently, and specimens for analysis were taken from it at intervals of about twelve hours. The following were the results:

Number of analysis.	Weight of residue taken for analysis. Gram.	Weight of ammonia found. Gram.	Percentage of ammonia found.
I.	0.4795	0.0767	15.99(T)
II.	0.3571	0.0514	14.37(T)
	0.4461	0.0642	14.39(T)
III.	0.3698	0.0538	14.54(T)
	0.7507	0.1100	14.65(T)
IV.	0.2948	0.0413	14.01(T)
	0.4869	0.0682	14.01(T)

It is interesting to note that the specimens, the analyses of which have just been given, were all "apple-green" in color.

The behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated in dry air at 100°, 125°, and 149° C. seems to be characteristic of salts whose molecules contain copper sulphate combined with water. We have found it impossible to prepare pure $CuSO_4 + H_2O$ and $CuSO_4$ from the pentahydrate by heating it in dry air.

In dehydrating the pentahydrate at 100° C. we used an air-bath consisting of a large glass tube encased in a tin condenser-jacket, through which steam was passed. The following is the record of an experiment in which some of the pure pentahydrated copper sulphate, the analysis of which has been given on page 264, was heated in this air-bath in a current of dry air:

	Gram.
Weight of pentahydrate taken	0.7629
" after five hours heating	0.5441
" " four hours more	0.5440
" " six " "	0.5441
" " three " "	0.5442
" " one hour at 105° C.	0.5441
" " three hours at 105°–110° C.	0.5441

The percentage loss in weight was 28.69 per cent, whereas the calculated percentage loss in weight when $CuSO_4 + 5H_2O$ decomposes into $CuSO_4 + H_2O$ is 28.85 per cent. The material in the boat, after heating, was brownish all over the surface and pale-blue beneath the surface. We then heated another specimen of the pentahydrate in a Victor Meyer bath, using alcohol in the bath. When the residue had become constant in weight at 78° C. it was found to have been formed from the pentahydrate by a percentage loss in weight of 28.55 per cent; calculated, 28.85 per cent. This residue was tinged with brown, and when heated in dry air at 100° C. it became decidedly brownish.

Several attempts to prepare anhydrous copper sulphate from the pentahydrate by heating it in dry air at the lowest temperature given by Graham[1] (220° C.) resulted similarly in browned products and varying losses in weight, as is shown by experiments I. to III. in the following:

Number of experiment.	Weight of pentahydrate heated. Grams.	Weight of residue after heating. Gram.	Percentage loss in weight found.	Percentage loss in weight calculated.
I.	0.4416	0.2839	35.71(T)	36.69
II.	0.6185	0.3961	35.95(T)	
III.	0.3974	0.2533	36.26(T)	
IV.	1.1253	0.7199	36.03	
V.	1.1067	0.7084	35.99	

Experiments IV. and V. were carried out by heating to constant weight at 280° C.

In view of these experiments, we are of the opinion that a molecule containing copper sulphate combined with water cannot undergo change without secondary reactions taking place between the water and the copper sulphate, giving mixed products. By this view the behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated in dry air at 100°, 125°, and 149° C. is readily explained, as well as our experiences in dehydrating pentahydrated copper sulphate. That mixed products are always formed in this dehydration we find also very clearly shown by the experiments of Naumann,[2] the view as readily accounts for the failure of Mallaert's method for the preparation of the salt $CuSO_4 + 4NH_3 + H_2O$, and for the fact that basic salts are formed when ammonia acts on the salt $CuSO_4 + 4NH_3 + H_2O$.

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[1] Ann. Chem. (Liebig), 30, 147.

[2] Ber. d. chem. Ges., 7, 2, 1573.

(*D*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 203° C.*—We heated at 200° to 203° C. residues previously obtained at 125° and 149° C. We used the same bath as was used in the experiments at 125° and 149° C., but provided it with a Reichert gas-regulator so arranged that the mercury in it closed an electric circuit and rang a bell as soon as the temperature reached 202° C. In the two following experiments the residues were heated about eight hours before their weights became constant:

Original weight of salt heated. Gram.	Weight of of residue after heating. Gram.	Percentage loss in weight.	Percentage loss calculated if $CuSO_4 + NH_3$ is formed.
1.0788	0.7739	28.26	28.15
0.5498	0.3944	28.25	

The following weighings of the second product prove that its weight was constant for the given conditions:

	Gram.
Weight of salt before heating	0.5498
" after twenty hours at 200°–203° C.	0.3945
" " thirty-nine hours at the same temperature	0.3944

As would be expected, the results show that the product is not a definite chemical compound.

In the above experiments the appearance of the products was perfectly uniform, and their color light-blue, but in other experiments at the same temperature, in which the heating was not even throughout the length of the boat, mixtures of substances with colors from sky-blue to pale-green and having perfectly constant weight, were obtained. The following description of one such experiment illustrates the course followed in raising the temperatures and also the constancy in weight of the mixed residues in these experiments:

Heated two hours at 125° C.
" five hours below 130° C.
" four hours at 155° to 170° C.
" three hours at 170° to 190° C.
" two hours at 200° to 203° C.

	Gram.
Weight of residue was then	0.3032
Heated four hours at 200° to 203° C.	
Weight of residue	0.3030
Heated three hours at 200° to 203° C.	
Weight of residue	0.3030
Original weight of $CuSO_4 + 4NH_3 + H_2O$ was	0.4196
Percentage loss in weight, 27.79	

In four such experiments entirely similar mixed products were obtained, the losses in weight ranging from 27.09 to 27.79 per cent.

(*E*) *Behavior of the Salt* $CuSO_4 + 4NH_3 + H_2O$ *at 260° C.*—Kane has stated that anhydrous copper sulphate is formed when this salt is heated at 260° C. We tried several such experiments, all of which yielded brown products. The following analyses of three of these products for copper show that they were not anhydrous copper sulphate:

Percentage of copper found in residue.	Percentage of copper calculated for $CuSO_4$.
39.51	39.83
40.13	
39.51	

V. Properties of Aqueous Solutions of the Salt $CuSO_4 + 4NH_3 + H_2O$.

1. All solutions of the salt have quite a strong odor of ammonia. The tension of ammonia over a solution of copper sulphate, to which an excess of ammonia has been added, is less than over an aqueous solution of ammonia of the same concentration. If the tension in a given case be corrected by subtracting from the total tension that due to 4 gram-molecules of ammonia for every gram-atom

of copper present, the corrected tension is less than that actually observed. Locke and Forssell have recently[1] interpreted this excess of tension as due to the lesser solubility of ammonia in cuprammonium sulphate solutions than in water. They assume that the complex cuprammonium salt and the complex cuprammonium ion do not affect the tension at all by their dissociation.

It is true that if the salt underwent any considerable molecular dissociation with loss of ammonia, we could not have kept it in a bell-jar over lime for more than a year without decomposition (see page 267), and it would lose weight in a vacuum over sulphuric acid much faster than we found that it did (see page 268). On the other hand, the facts that the salt smells strongly of ammonia at once when moistened, that the decomposition by water is so rapid that the salt cannot be dried between filter-papers, and that all of its solutions smell strongly of ammonia, are not in accord with their assumption. There is sufficient reason in these facts to believe that the excess tension of ammonia is due at least in part to the hydrolytic dissociation with loss of ammonia of the complex salt or its electrolytic dissociation-products.

2. The salt gives a clear solution when water is poured gradually upon it, but if the addition of water is continued a permanent precipitate is formed at about N/20 to N/25[2] concentration. When a solution of the salt is dropped into water a permanent precipitate is formed at once.

3. A N/10 solution of the salt after standing a couple of days in a tightly closed vessel begins to deposit a crystalline blue solid ; this continues for weeks.

4. If a current of air (free from carbon dioxide) is passed through a N/10 solution of the salt, ammonia is removed by the air, and after about twenty-four hours a finely crystalline blue deposit begins to form on the walls of the vessel. This precipitate increases in bulk throughout a long period of time.

5. When a solution of the pure salt, or of the pure salt with

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[1] This JOURNAL, 31, 268 (1904).

[2] These concentrations are fractions of " molecular normal."

an excess of ammonia, is titrated into acids the precipitate at first formed redissolves until a definite limit is reached, when the precipitate becomes permanent. This point at which the precipitate becomes permanent is very sharp, and in a solution of the pure salt lies very close to the point of neutrality of the liquid. This point is also independent of the anion of the acid used, at least in the case of strong acids. The following figures present a comparison of the weights of different acids used up by 1 cc. of a given salt solution with the weights of the same acids calculated as just equivalent to the ammonia of the salt in 1 cc. of the given solution. They also show that the nature of the anion of the acid is without effect.

	Calculated. Gram.	Found. Gram.
HCl	0.0147	0.0146
H_2SO_4	0.0198	0.0192
HNO_3	0.0255	0.0252

6. Pure copper sulphate is very approximately neutral to methyl orange indicator. This indicator can be used to determine the alkalinity of the liquids in which the permanent precipitate described in (5) is formed. The following results show the definiteness of the methyl orange end-reaction under these conditions, as well as that of the reaction indicated by the permanent precipitate. They also show that the precipitate forms in a feebly alkaline solution :

Volume of acid required by 1 cc. cuprammonium solution to give permanent precipitate. cc.	Volume of acid required by same to give neutrality to methyl orange. cc.
1.93	1.98
1.94	1.98
1.94	1.98
2.32	2.38
2.32	2.38
2.33	2.38
3.03	3.12
3.04	3.11
3.04	3.11

7. The reaction indicated by the permanent precipitate is affected by the presence of ammonia, as is also the neutralization indicated by methyl orange. In neither case is the effect proportional to the ammonia added. The following results set forth these points :

Number of solution.	Molecular concentration of solution with respect to copper.	Ratio Cu : NH_3 in solution.	Ratio Cu : $\overset{+}{\mathrm{H}}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{\mathrm{H}}$ at time of neutrality to methyl orange.
I.	N/9.87	1 : 4	1 : 3.88	1 : 3.97
II.	N/9.95	1 : 4.82	1 : 4.65	1 : 4.77
III.	N/9.55	1 : 6.06	1 : 5.84	1 : 5.99

8. In a given solution both of these reactions change with time. The total alkalinity diminishes and the alkalinity, at the moment when the permanent precipitate is formed, increases. The presence of an excess of ammonia does not prevent this displacement of the two end-reactions with time. Thus after solution I., above, had deposited some of the blue solid mentioned in (3) the alkalinity at the moment of permanent precipitation had increased from 0.09 to 0.12 gram-equivalents of $\overline{\mathrm{OH}}$ to each gram-equivalent of copper present. The following results show the changes with time in solution III., above. The time was forty-eight hours. They also show that the excess of ammonia present did not stop these changes :

Number of solution.	Concentration with respect to copper.	Ratio Cu : NH_3 in the solution.	Ratio Cu : $\overset{+}{\mathrm{H}}$ at time of permanent precipitation.	Ratio Cu : $\overset{+}{\mathrm{H}}$ at time of neutrality to methyl orange.
III.	N/9.55	1 : 6.06	1 : 5.84	1 : 5.99
III.	N/9.55	1 : 6.06	1 : 5.80	1 : 5.96

These experiments were conducted with the greatest care. The flasks were carefully calibrated by weighing the water they contained at definite temperatures, and the burettes were calibrated by a method devised recently by one of us.[1] The solutions were made by weighing the flasks first dry and empty, and again after the salt had been introduced and the flasks stoppered. Significant differences in temperature were corrected for.

The properties of solutions of the salt $CuSO_4 + 4NH_3 + H_2O$ indicate that the salt is decomposed by water with the partial separation of ammonia from the combination in which it is held by the salt in the dry condition (see 1, 2, and 3 above). This decomposition is probably an hydrolysis (see 6). In solutions of the pure salt it proceeds at least as far as the formation and precipitation of basic salts (see 2, 3, and 5). In solutions of the salts, even though they may contain an excess of ammonia, the concentration of hydroxyl ions undergoes changes throughout a considerable period of time (see 8). These changes are hastened or retarded by the removal or addition of ammonia (see 4 and 7), but the effects of the ammonia do not bear any simple relation to the concentration of the ammonia (see 8).

The formula $CuSO_4 + 4NH_3 + H_2O$ does not correctly represent the salt. If this formula were correct, the addition of 1 molecule of the salt to 4 equivalents of acid would produce a clear solution containing copper sulphate and ammonium salts and the products of their electrolytic dissociation, and would not produce a permanent precipitate (see 5).

VI. Summary.

1. We have shown the method of Fresenius and the "suggestion" of Küster and Thiel to be unreliable in the quantitative separation of sulphuric acid from copper. We have described a satisfactory method for the separation and for the determination of ammonia and water in a mixture of the vapors of the two. The conditions under which reliable results can be obtained in the complete analysis of cuprammonium sulphates have been worked out and have been stated.

2. The preparation of the salt $CuSO_4 + 4NH_3 + H_2O$ has been described, and a method of drying it and keeping it in-

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[1] This JOURNAL, **30**, 96 (1903).

definitely in an analytically pure condition has been given. Its composition has been proved by complete analyses. Other products described as this cuprammonium sulphate by Malaert and Bouzat have been shown to be mixtures. The method of drying hydrated cuprammonium salts over sticks of potassium hydroxide and a very little ammonia water, used recently by Kohlschütter, has been shown to alter the composition of the salts.

3. The properties of the pure dry salt $CuSO_4 + 4NH_3 + H_2O$ have been studied, and it has been shown that its molecular dissociation with loss of ammonia must be very slight. Its solubility at 21° to 22° C. has been determined. The action of dry ammonia upon the salt has been studied, and it has been shown that under the given conditions the replacement of the molecule of water in the salt by a molecule of ammonia described by Latschinoff does not take place without other reactions setting in, producing mixed products.

4. We have studied the behavior of the salt $CuSO_4 + 4NH_3 + H_2O$ when heated at 100°, 125°, 149°, 203°, 260° C., and have shown that the products in all cases were mixtures. The definite chemical compounds

$$CuSO_4 + 2NH_3 \qquad \text{and} \qquad CuSO_4 + NH_3$$

described by Kane do not exist as such; if they are formed at all they are mixed with other products. We have studied the behavior of pentahydrated copper sulphate at 78°, 100°, 220°, and 260° C. and have shown that the dehydration-products were mixtures. We have shown that the action of ammonia on pentahydrated copper sulphate produces a mixture and that this is also true when ammonia acts on the salt $CuSO_4 + 4NH_3 + H_2O$, even though both reactions take place at ordinary temperatures. We are of the opinion that a solid compound containing both copper sulphate and water cannot undergo change without other reactions between these two constituents taking place, giving rise to mixed products. For this reason, results of experiments on record in which solid hydrated compounds of copper sulphate have been heated, or treated with a gas, or changed in other ways (while still solid) are, *ipso facto*, open to doubt. The most recent work to which this applies is that of Latschinoff.

5. Properties of aqueous solutions of the salt

$$CuSO_4 + 4NH_3 + H_2O$$

have been described that show that the system

$$\{CuSO_4 + 4NH_3 + H_2O\} + xH_2O$$

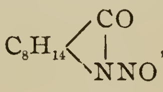
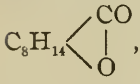
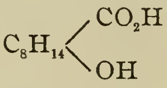
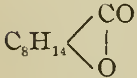
as found in a solution of the salt is in an unstable condition, beginning with its existence to undergo a change that continues for a long time and that it is in some cases not complete while the system remains homogeneous. The change which results in the precipitation of basic salts is hastened by the removal of ammonia and by great dilution. We have found that the change in the solutions can be followed readily by taking advantage of the facts that cuprammonium sulphate solutions titrated into acids give a definite end-reaction characterized by the formation of a permanent precipitate, and that copper sulphate solutions are practically neutral to methyl orange indicator. The results obtained in this way do not permit of a satisfactory interpretation.

Because of the changes in solutions of this cuprammonium sulphate that continue for a considerable time, deductions of a general character drawn from studies of cuprammonium sulphate solutions (in water) must be considered doubtful except in cases where it has been shown that the measurements were made after equilibrium had been established in the solutions. The most recent work to which this applies is that of Dawson and McCrea and of Locke and Forssell.

Chemical Laboratory,
Bryn Mawr College,
April, 1904.

THE DECOMPOSITION OF NITROSO COMPOUNDS.

By William A. Noyes and René de M. Taveau.

Bredt has stated[1] that when the nitroso derivative of the anhydride of dihydroaminocampholytic acid,  $C_8H_{14}\left\langle\begin{array}{l}CO\\ |\\ NNO\end{array}\right.$, is decomposed by treatment with sodium hydroxide a lactone,  $C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ O\end{matrix}\right.$, is formed. Blanchard and one of us, on repeating the experiment,[1] probably with somewhat different conditions, as Bredt gives no details, obtained as the chief products of the decomposition active α-campholytic acid and dihydrohydroxycampholytic acid, with little or none of the lactone. More recently Bredt has prepared the nitroso derivative of the anhydride of aminolauronic acid and states[2] that on decomposing this with sodium hydroxide a lactone is also formed. He has, apparently, overlooked the fact that the same lactone was obtained in an impure condition by one of us[3] some years ago and called isocampholactone. In the decomposition of the lauronic acid, or its ester with nitrous acid, four products are found: Isolauronolic acid, $C_8H_{13}CO_2H$; hydroxylauronic acid,  $C_8H_{14}\left\langle\begin{matrix}CO_2H\\ \\ OH\end{matrix}\right.$; isocampholactone,  $C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ O\end{matrix}\right.$; and a hydrocarbon, C_8H_{14}.

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[1] Ann. Chem. (Liebig), **314**, 392. (1900)

It seems, therefore, that dihydroaminocampholytic acid and aminolauronic acid each give two hydroxy acids on treatment with nitrous acid, and that one of each of these pairs of acids forms a lactone while the other does not. It seems of interest to determine whether the hydroxy acid which forms the lactone and the other one derived from the same amino acid which forms no lactone are stereomeric or place isomers. It was also of interest to determine whether the decomposition of the nitroso derivative of the anhydride of aminolauronic acid gives only the lactone, as seems to be implied in Bredt's statement, or if it gives also the other compounds referred to above. While our work has only been carried far enough to answer the latter question, we have incidentally discovered a new class of compounds formed when the decomposition takes place in the presence of an alcoholic solution of sodium hydroxide. The study of these compounds is far from complete, but as we can no longer continue the work together it seems desirable to publish the results already obtained.

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[1] This JOURNAL, **26**, 284.

[2] Ber. d. chem. Ges., **35**, 1291.

[3] This JOURNAL, **17**, 432.

Preparation of Camphoramidic Acids.—Considerable experience in the preparation of the camphoramidic acids has been gained since the details of preparation were last given[1] and as they furnish the starting-point for the preparation of a large number of important derivatives of camphoric acid it appears worth while to give the methods now used. One hundred grams of finely powdered camphoric anhydride are placed in a 500 cc. bottle, 150 cc. of strong ammonia (0.90) added, the stopper of the bottle firmly tied down, and the mixture shaken vigorously till the anhydride has passed into solution. The solution is then cooled rapidly, but thoroughly, and the ammonium salt of the α-camphoramidic acid, which separates, filtered off on a plate and washed twice with a small amount of a 10 per cent solution of ammonium chloride. To the filtrate from the ammonium salt is added a 50 per cent solution of sodium hydroxide, which causes the separation of a considerable amount of the sodium salt of the β-camphoramidic acid. This is filtered off on a hardened filter and washed twice with a small amount of a 10 per cent solution of sodium hydroxide. The free amidic acids are obtained by dissolving the respective salts in warm water, cooling, and precipitating with hydrochloric acid. The acid should be added very carefully, with vigorous stirring, till the amidic acid begins to separate in crystalline form. If the mineral acid is added too rapidly, the acid will separate as a gummy mass, which is less pure. The yield is 45 to 55 per cent of the α-acid and 20 to 25 per cent of the β-acid.

The hydrochloride of aminolauronic acid was prepared from the α-camphoramidic acid[2] and the anhydride was prepared by distilling the hydrochloride with lime.[3] The anhydride may also be prepared by heating the free amino acid to 300°

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[1] This JOURNAL, **16**, 502.

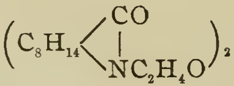
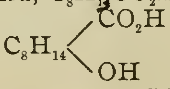
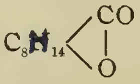
[2] *Ibid.*, **16**, 506.

[3] *Ibid.*, **16**, 507.

in an oil-bath. It boils at 285°. The isomer derived from dihydroaminocampholytic acid boils at 285° to 287°.[1] The rotation of a 7 per cent solution in absolute alcohol is $[\alpha]_D = -60°.1$ at 26°.

The nitroso compound was prepared by dissolving the anhydride in dilute hydrochloric acid and adding a little more than the calculated amount of sodium nitrite.[2] The nitroso compound was crystallized from alcohol or ligroin. It melts at 138° to 139°. The racemic form also melts at 138°.[3]

When the nitroso compound is moistened with strong alcohol and a 10 per cent solution of sodium hydroxide is added, while the whole is cooled with ice-water, it decomposes with the formation of the various products in approximately the following proportion :

	Grams.
Nitroso compound taken	19.5
Hydrocarbon, C_8H_{14}	2.5
Condensation-product,  $\left(C_8H_{14}<\begin{matrix}CO\\ \vert\\ NC_2H_4O\end{matrix}\right)_2$	5.0
Isolauronolic acid, $C_8H_{13}CO_2H$	1.2
Hydroxy acid,  $C_8H_{14}<\begin{matrix}CO_2H\\ \\ OH\end{matrix}$	1.5
Isocampholactone,  $C_8H_{14}<\begin{matrix}CO\\ \vert\\ O\end{matrix}$	1.3

These products were separated essentially as follows : After the decomposition of the nitroso compound was complete the mixture was heated in a current of steam, which carried over the hydrocarbon. This was easily separated from the aqueous distillate. The oily residue in the distilling-bulb sometimes solidified and consisted mainly of the condensation-product. By acidifying the alkaline solution separated from the condensation-product, the isolauronolic acid, lactone, and hydroxy acid were liberated and were then extracted from the solution with ether. After distilling the ether, the lactone and isolauronolic acid were driven over with steam, leaving the hydroxy acid behind. The lactone and isolauronolic acid were extracted from the distillate with ether, and after distilling the ether, were separated by a solution of potassium carbonate, which dissolves the acid and not the lactone.

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[1] This JOURNAL, **16**, 504.

[2] Bredt : Ber. d. chem. Ges., **35**, 1291.

[3] Noyes and Warren : This JOURNAL, **28**, 486.

There was evidently considerable loss in the separation of the products and the results cannot be considered accurate, but it is evident that the hydroxy acid may be considered the direct product of the decomposition with as much reason as the lactone.

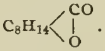
The hydroxy acid may be distilled under diminished pressure without decomposition, boiling at 180° to 185° under a pressure of 25 mm. It is evident that this is the same hydroxy acid as that whose ester is formed by the action of nitrous acid on the ethyl ester of aminolauronic acid. Hydroxydihydrocampholytic acid, the isomer which corresponds to this but which has the positions of the hydroxyl and carboxyl reversed, also forms no lactone.

Configuration of the Lactone.—It is generally assumed that in ordinary camphoric acid, which forms an anhydride, the carboxyl groups are both on the same side of the plane of the ring, while the isocamphoric acid is assumed to be the trans form. The fact that ordinary camphoric acid, dihydroaminocampholytic acid, dihydrohydroxycampholytic acid, and α-bromdihydrocampholytic acid are all dextrorotatory and that their rotatory power, except that of the last, is of much the same order of magnitude, is considerable evidence that all possess a similar configuration. If this is true and all are *cis* compounds, it seems probable that isocampholactone and the lactone derived from dihydroaminocampholytic acid are *trans* compounds. It would follow from this that cyclic hydroxy acids having carboxyl and hydroxyl in the 1,3-position form lactones only when the groups are *trans* with regard to each other. The close agreement in the specific rotation of the anhydride of aminolauronic acid and of isocampholactone indicates that these have a similar configuration, however, and the evidence is, at present, conflicting. The matter is of considerable interest, and it is our intention to give it further study. Perkin and Thorpe[1] have recently described a cyclic γ-hydroxy acid which forms no lactone, and they refer to other similar cases.

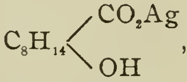
Isocampholactone.—As already stated, this was discovered by one of us some years ago, but it was obtained only in small amount and in an impure condition, so that the compound was not analyzed and the melting-point was found nearly 10° too low. Bredt gives the melting-point as 32°, and we have found the same. He gives no analyses. We found :

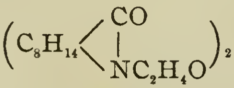
I. 0.1336 gram substance gave 0.3426 gram CO_2 and 0.1086 gram H_2O.

II. 0.1218 gram substance gave 0.3105 gram CO_2 and 0.0988 gram H_2O.

	Calculated for  $C_8H_{14}{<}\begin{matrix}CO\\ \vert\\ O\end{matrix}$.	Found. I.	Found. II.
C	70.11	69.93	69.53
H	9.11	9.18	9.08

The substance is laevorotatory. For a 5 per cent solution in alcohol $[\alpha]_D = -60^\circ.7$.

The silver salt,  $C_8H_{14}{<}\begin{matrix}CO_2Ag\\ OH\end{matrix}$, of the hydroxy acid corresponding to the lactone was prepared by heating the latter with a little more than the calculated amount of alcoholic potash for an hour and a half, distilling off the alcohol, exactly neutralizing with nitric acid and precipitating with silver nitrate. The salt gave 38.82 per cent of silver. Calculated, 38.68 per cent.

The condensation-product,  $\left(C_8H_{14}{<}\begin{matrix}CO\\ \vert\\ NC_2H_4O\end{matrix}\right)_2$, is formed when the nitroso compound is moistened with alcohol and decomposed by adding an aqueous solution of sodium hydroxide, or better, by decomposing the nitroso compound by an alcoholic solution of sodium hydroxide. The substance was crystallized from alcohol and from ligroin. From the latter solvent it separates in large, well-formed plates having a faint yellow color. It melts at 104°. It is almost insoluble in water. It dissolves slightly in dilute hydrochloric acid and may be reprecipitated by ammonia, the reprecipitated substance melting still at 104°. The analysis gave :

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[1] J. Chem. Soc. (London), 85, 131.

	Calculated for $(C_{11}H_{18}NO_2)_2$.	Found. I.	II.
C	67.28	66.91	67.00
H	9.25	8.93	9.13
N	7.16	7.50	7.51

An amount weighing 0.1774 gram dissolved in 15.67 grams of benzene gave a lowering of the freezing-point of 0°.166, and 0.2445 gram gave a lowering of 0°.229. 0.1904 gram dissolved in 39.42 grams of benzene gave a rise in the boiling-point of 0°.390. These correspond to the values 334, 348, and 343 for the molecular weight. Calculated for $(C_{11}H_{18}NO_2)_2$, 392.4. The agreement is not satisfactory, but the results indicate that the substance contains a doubled molecule as compared with the original substance. It is also apparent that the ethyl alcohol used has taken part in the formation of the compound.

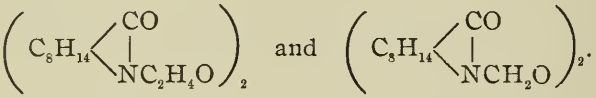
This last fact suggested the use of a solution of sodium hydroxide in methyl alcohol. When the nitroso compound is decomposed by such a solution, a similar condensation-product having the formula $(C_{10}H_{16}NO_2)_2$ is formed. This crystallizes from ligroin in leaflets, which melt at 99°. It is slightly soluble in acids and is precipitated from the solution by ammonia. The analysis gave :

	Calculated for $(C_{10}H_{16}NO_2)_2$.	Found. I.	II.
C	65.86	65.87	65.57
H	8.86	8.40	8.49
N	7.70	7.69	....

A solution of 0.2311 gram in 20.68 grams of benzene gave a freezing-point lowering of 0°.160, and 0.3598 gram gave a lowering of 0°.286. These correspond to 341 and 327 for the molecular weight. Calculated, 364.3.

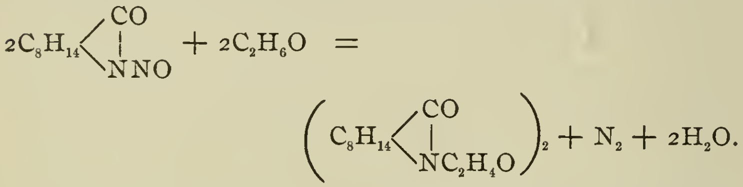
Experiments were also tried with isoamyl alcohol and with allyl alcohol. Condensation-products were evidently formed in both cases but these could not be made to crystallize.

When these formulas are examined it is seen that they correspond to the nitroso compound less the nitroso group and with the addition of a molecule of acetaldehyde or formaldehyde, thus:



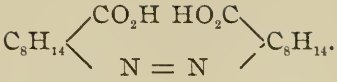
$$\left(C_8H_{14}\Big\langle\begin{matrix}CO\\ |\\ NC_2H_4O\end{matrix}\right)_2 \text{ and } \left(C_8H_{14}\Big\langle\begin{matrix}CO\\ |\\ NCH_2O\end{matrix}\right)_2.$$

The following reaction would explain these formulas:



$$2C_8H_{14}\Big\langle\begin{matrix}CO\\ |\\ NNO\end{matrix} + 2C_2H_6O = \left(C_8H_{14}\Big\langle\begin{matrix}CO\\ |\\ NC_2H_4O\end{matrix}\right)_2 + N_2 + 2H_2O.$$

So far as we are aware, no similar decomposition of a nitroso compound has been observed by others. There is some analogy with the formation of acetaldehyde by the action of diazo compounds on ethyl alcohol. It is hoped that further study may lead to a generalization of the reactions and that it may also throw further light on the structure of these compounds.

After filtering off the condensation-product resulting from the action of the methyl alcoholic sodium hydroxide on the nitroso compound, the solution was acidified. This caused the precipitation of a white, solid acid instead of the usual oily mixture. This was washed with ether, in which it is nearly insoluble, and crystallized from alcohol. The amount was about 11 per cent of the weight of the nitroso compound. The substance melts at 327° to 328° (corr.) A nitrogen determination gave 8.32 per cent. Theory requires for the formula $(C_9H_{15}NO_2)_2$, 8.29 per cent. 0.1022 gram required 6.19 cc. of N/10 potassium hydroxide for neutralization. Theory requires for a bibasic acid, having the formula $(C_9H_{15}NO_2)_2$, 6.04 cc. It seems possible that the acid is an azo compound having the structure  $C_8H_{14}\genfrac{}{}{0pt}{}{CO_2H\quad HO_2C}{N = N}C_8H_{14}$. It is hoped to study this compound further.

Johns Hopkins University,
May, 1904.

REVIEWS.

Die Kathodenstrahlen. Von G. C. Schmidt. Braunschweig: Druch von Friedrich Vieweg und Sohn. 1904.

The cathode rays, which were first described by Hittorf more than thirty-five years ago, and brought into prominence chiefly by the brilliant experiments of Crookes, stubbornly refused to give any experimental evidence of their true nature until the study of the ionization of gases by X-rays opened up new lines of attacking the problem. Crookes regarded the rays as flight of molecules driven from the cathode at high velocity and having mean free paths measured in centimeters instead of thousandths of a millimeter. He regarded this condition as a fourth state of matter, to which he gave the name ultra-gaseous. The German physicists however, almost without exception, regarded the rays as a phenomenon of the ether, a view which was strengthened by the failure of Hertz to obtain any trace of a deflection in an electrostatic field, which was to be expected if the rays consisted of charged molecules or atoms, and the experiments of Lenard on the transmission of the rays through aluminium foil.

Though Crookes' original hypothesis has been shown to be untenable, a modification of it, suggested by Schuster, is at the present time almost universally held, the velocities, masses, and charges of the electrons which constitute the rays having been determined with considerable accuracy.

The wide applications which have been made of the electron theory in the domains of physics, chemistry, meteorology, and astronomy, together with the physiological effects of the different types of radiation, make the cathode rays, and the phenomena which accompany them, of interest to workers in almost every branch of science. Professor Schmidt has given us a very concise résumé of the most important work which has been done in clearing up the mystery which has so long hung around the cathode rays, which will prove useful to all who are interested in the development of the modern conception of the "Electron."

The treatment is wholly non-mathematical and is well illustrated with diagrams and cuts. After discussing the various types of apparatus used in the production and study of the cathode rays, the author gives a short review of the various theories which different experimenters have advanced, and the development of the present theory by Schuster, whose theoretical speculation he considers as far eclipsing those of any of his predecessors.

The behavior of the rays in magnetic and electrostatic fields is very fully discussed, together with the methods by which the masses of the moving electrons and their velocities are determined from observations of the deflections of the rays.

In the chapter on the various methods of producing cathode rays, the author omits mention of the fact that Merritt made an independent discovery of the generation of the rays by the illumination of metal surfaces by ultra-violet light, though his paper did not appear until some months after Lenard's. This is doubtless an oversight, for the book is conspicuously free from the tendency shown by some writers to minimize the value of, or ignore completely, work done in other countries. This is especially noticeable in the frequent tribute which he pays to the work of Crookes', which German writers, as a rule, do not seem to have appreciated. While it is true that many of the observations which he made had been previously recorded by Hittorf, he was the first to draw the attention of the world at large to the cathode rays and popularize them by a series of most spectacular experiments, which for the past quarter of a century have been yearly repeated in practically every physical laboratory in the world.

It is to be regretted perhaps that the author has devoted so little space to the emission of the rays by radioactive substances, these cases being the ones upon which interest is chiefly centered at the present time.

The book closes with an allusion to the almost prophetic remark which Crookes made in one of his earlier papers, to the effect that, in his opinion, the greatest scientific problems of the future would find their solution in the realm of "Radiant matter." The establishment of the fact that the disintegration of the radium molecule is accompanied by the emission of types of radiation similar in every respect to those occurring in vacuum tubes seems almost like a verification of this prediction. R. W. W.

IMMUNE SERA: HÆMOLYSINS, CYTOTOXINS, AND PRECIPITINS. By A. WASSERMANN, M.D., University of Berlin. Authorized translation by CHARLES BOLDUAN, M.D. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 77.

Dr. Bolduan has rendered a real service in translating this little volume of Wassermann, for, of the various summaries of the recent work in this complicated field, this is perhaps the most satisfactory and readable. The title in German is "Hämolysine, Cytotoxine und Präcipitine;" the addition "Immune Sera" in the translation is in a way misleading, for the scope of the work is by no means as broad as implied, and the reader who hopes to find in this little volume a treatise on immunity with a discussion of the various anti-plague, anti-typhoid, anti-diphtheria sera, etc., will be disappointed.

More than two-thirds of the book is taken up with a discussion of the hæmolysins—those substances occurring normally in the serum, and in virtue of which it is capable of dissolving the blood corpuscles of certain other animals. The interest attaching to these bodies comes largely from the fact that an immunity reaction can be obtained with them, *i. e.*, if the blood corpuscles of one animal (A) be injected into another animal (B) the serum of the latter acquires the power of dissolving the corpuscles of A. The results are thus similar to those obtained in many cases with bacteria, and as the experiments can be performed in test-tubes and permit of great accuracy, they offer exceptional opportunities of investigating the laws governing the production of immune sera in general. The work of Ehrlich, which has contributed so largely not only to the collection, but still more to the coordination of facts, is fully discussed in relation to his "side-chain" theory of immunity.

On page 19 it is stated that Ehrlich formulated the "side-chain" theory in order to explain the production of antitoxin and other specific anti-bodies. As a matter of fact the side-chain theory was proposed by Ehrlich nearly twenty years ago, entirely independently of any theory of immunity; through it Ehrlich sought to explain the processes of oxidation in the body. Thus Ehrlich's side-chain theory has a wider biological significance than the reader would be led to suppose from the above statement.

Cytotoxins (other than the hæmolysins) are discussed in the second section. Specific reaction substances can be obtained towards leucocytes, spermatozoa, epithelial, and other cells in the same way as hæmolysins are obtained.

In the third section the author discusses the subject of "precipitins"—those "anti-bodies" obtained by the injection of various kinds of proteids into animals of another species; the serum of the latter acquires the property of forming a precipitate with the form of proteid injected. By this method, in the development of which Wassermann has taken such an important part—it is possible to determine the species of animal from which a given specimen of proteid (*e. g.*, that of human blood) has been obtained, results which seemed unobtainable by any ordinary chemical method. It is perhaps unnecessary to remark that the chemical nature of these "immune bodies" (hæmolysins, cytotoxins, and precipitins) is unknown beyond the fact that they seem to belong to the group of proteids.

The translation has been well done; the advisability of translating "Zwischen-Körper" by "inter-body" may, however, be questioned, the translation "intermediary body" having received the sanction of such authorities as Meltzer, Welch, and Flexner.

To the specialist who desires the very latest developments in this subject, the book cannot be so highly recommended, for the German edition appeared two years ago and contains none of the work published since 1901. Since that time many important papers have appeared, but the fundamental work (*e. g.*, that of Bordet and Ehrlich) is discussed fully and clearly, and what has appeared since has modified this but little. R. H.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By FREDERICK H. GETMAN, PH.D., Fellow by Courtesy in the Johns Hopkins University, Carnegie Research Assistant. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 241.

This little laboratory guide in physical chemistry will prove to be useful in American and English laboratories, wherever physical chemistry is taught. While several excellent manuals have been published in German there is, up to the present, nothing in English that is adapted to general use.

The subject is treated under thirteen heads: Weighing; Volume and Density; Viscosity and Surface-tension; Solubility; Thermometry; Melting- and Boiling-points; Calorimetry; The Spectroscope; Electrical Units; Resistance; Electromotive Force; Measurement of Current; Measurement of the Dielectric Constant; Chemical Kinetics; and Tables.

Under the last-named head are included quantities which are in constant use in the laboratory.

The book is well-illustrated and well-printed. Omission of letters in headings as on pages 64, 101, and 215 can be easily corrected. The work is heartily recommended to all who are interested in physical-chemical measurements. H. C. J.

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AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF THE 1,3,5-TRIIOD-2,4-DINITROBENZOL.

BY C. LORING JACKSON AND J. F. LANGMAID.

This triioddinitrobenzol was described by Istrati and Georgescu,[1] in 1892, as they obtained it from their triiodbenzol, melting at 182° to 184°, made by heating together benzol, iodine, and sulphuric acid. They did not, however, determine its structure, which was done in 1900 by G. E. Behr and one of us,[2] who proved that it had the following constitution: $I_3$1,3,5.$(NO_2)_2$2,4. In 1901 Willgerodt and Arnold,[3] who apparently had overlooked the paper by Behr and one of us, in an extended paper on iodine compounds of benzol confirmed this result, proving its constitution in a different way.

In the paper just cited as issued from this laboratory in 1900, it was announced that the behavior of triioddinitrobenzol with various agents would be studied, and the present paper contains an account of the work done in this direction.

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[1] Buletinul Soc. Sci. Fiz. Bucuresci, **1**, 62 (1892).

[2] This JOURNAL, **26**, 55 (1901).

[3] Ber. d. chem. Ges., **34**, 3343 (1901).

This research belongs to a series undertaken for the purpose of studying the anomalous replacement of halogen atoms by hydrogen in aromatic compounds, and has added three more cases of the sort to the rather meager list at present known. Thus, triioddinitrobenzol is converted by hot sodic ethylate into dinitroresorcine diethyl ether, $C_6H_2(OC_2H_5)_2(NO_2)_2$, by the replacement of 2 atoms of iodine by ethoxy groups and 1 by hydrogen, in this respect resembling closely the corresponding reaction with tribromdinitrobenzol,[1] from which the same substance is obtained as one of the principal products. The melting-point of the dinitroresorcine diethyl ether obtained from tribromdinitrobenzol was 133°, that of our product from triioddinitrobenzol only 130°, and all our attempts failed to raise it above this point, but analysis proved that it was $C_6H_2(OC_2H_5)_2(NO_2)_2$. Dunlap and one of us[2] obtained a dinitroresorcine diethyl ether melting as low as 126° by the action of fuming nitric acid on dibromresorcine diethyl ether. It is possible that this diethyl ether melting at 126° is the other isomer $(OC_2H_5)_2 1.3.(NO_2) 2.4$ (the one melting at 133° has the constitution $(OC_2H_5)_2 1.3(NO_2)_2 4.6$), but we think it more probable that some clinging impurity caused the differences in melting-points, and that Dunlap's and our substances are identical with the one that melts at 133°. The point can be finally settled only by further experiment.

With sodic malonic ester, too, a monoioddinitrophenylmalonic ester, $C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$, is formed, corresponding exactly to the $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$, made in the same way from tribromdinitrobenzol,[3] but, whereas the bromdinitrophenylmalonic ester is the principal product of the reaction, the iod compound is formed only in secondary amount, the principal product being diioddinitrobenzol, formed by the replacement of 1 atom of iodine by hydrogen. It can be inferred from this that iodine is more easily replaced by hydrogen than bromine, since no dibromdinitrobenzol was observed among the products of the action of sodic malonic ester on tribromdinitrobenzol. This is not unexpected, as we have not found any case, as yet, in which chlorine has been replaced by hydrogen under the influence of an alcoholate or sodic malonic ester, and it was to be expected that the tendency toward such replacement should vary with the atomic weights.

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[1] Jackson and Warren: This JOURNAL, 13, 170 (1891).

[2] *Ibid.*, 18, 122 (1890).

[3] *Ibid.*, 11, 94 (1889).

With sodic methylate the behavior of the triioddinitrobenzol was peculiar, as the principal product was the triiodnitroanisol, $C_6HI_3NO_2OCH_3$, whereas with tribromdinitrobenzol the reaction runs as with the ethylate, the principal products being $C_6HBr(OCH_3)_2(NO_2)_2$ and $C_6H_2(OCH_3)_2(NO_2)_2$. A small amount of another substance was obtained, which, to judge from a single analysis, was $C_6HI(OCH_3)_3NO_2$, and therefore showed a similarity to the first of the brom compounds given above, but it was not obtained in sufficient quantity for proper characterization. A compound analogous to this triiodnitroanisol is formed from tribromdinitrobenzol by the action of sodic ethylate,[1] $C_6HBr_3NO_2OH$, but the amount is only a few per cent of the whole product, so that it was not detected until the experiment was tried on a large scale. On the other hand, the triiodnitroanisol must have been a principal product, as it was isolated from a complex mixture obtained from comparatively small quantities of the triioddinitrobenzol. Tribromtrinitrobenzol[2] shows similar replacements of nitro groups with sodic ethylate, forming tribromdinitrophenetol, $C_6Br_3(NO_2)_2OC_2H_5$, or tribromnitroresorcine diethyl ether, $C_6Br_3(NO_2)(OC_2H_5)_2$. The most probable explanation of this difference between tribromdinitrobenzol and triioddinitrobenzol is that iodine is held more strongly than bromine by the carbon of the benzol ring, so that the nitro group offers less resistance to replacement than the iodine, and this view is confirmed by the impression conveyed to our minds by these experiments that the triioddinitrobenzol was more sluggish in its behavior with reagents than the tribromdinitrobenzol, but this impression needs confirmation by careful comparative experiments before it can be accepted as proved.

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[1] Jackson and Koch : This JOURNAL, **21**, 522 (1899).

[2] Jackson and Warren : *Ibid.*, **13**, 187 (1891).

In some of the experiments on the action of sodic malonic ester on the triioddinitrobenzol, a substance melting at 182° was obtained, which was proved to be an addition-compound of 2 molecules of diioddinitrobenzol with 1 of triioddinitrobenzol, $[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2$. Its nature was established by the analysis of the compound, by breaking it up into its constituents by crystallizations from alcohol and benzol, and by making it from its constituents in alcoholic solution. A similar addition-compound, $[C_6HBr_3(NO_2)_2]_2C_6Br_4(NO_2)_2$, was obtained by Moore and one of us.[1]

It must be borne in mind that all the experiments described in this paper were tried with small quantities of substance, and, therefore, in no case have we identified all the products of a reaction. The compounds described may, however, fairly be considered the principal products in each case.

EXPERIMENTAL PART.

Preparation of Triioddinitrobenzol.

The triiodaniline used was prepared by a modification of the process of Michael and Norton,[2] as follows: Ten grams of freshly distilled aniline were dissolved in 500 cc. of strong hydrochloric acid and the whole diluted to 5 liters. A stream of air charged with the vapor of chloride of iodine (ICl) was then passed through this solution until 54 grams had been added. The flask containing the chloride of iodine was heated to 60°. The whole of the precipitate was used in making the triiodbenzol, both the light-brown one formed at first and the flocculent buff-colored precipitate deposited later. The filtrate was used to dissolve the aniline for the next operation. Our yield by this process amounted to 50 to 70 per cent and is therefore better than that obtained by Behr and one of us.[3]

The triiodbenzol was prepared from the triiodaniline by a slight modification of the method given in the paper just cited. Ten grams of the triiodaniline were boiled with 125 cc. of benzol and 25 cc. of alcohol, and disregarding the undissolved portion, 5 cc. of commercial sulphuric acid were added, and after the mixture had cooled so that it was slightly warm, 5 grams of finely powdered sodic nitrite were added in small portions at a time, shaking the loosely corked flask after each addition. As soon as the evolution of nitrogen had slackened sufficiently the liquid was boiled for some time on the steam-bath, until a large part of the solvents had passed off. It was then allowed to stand over night, the deposit filtered out, and washed first with alcohol and afterwards with hot water. The yield with a gradual addition of the nitrite was better than when it was added all together, as recommended by Behr and one of us.[1]

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[1] Ber. d. chem. Ges., **21**, 1707 (1888).

[2] *Ibid.*, **11**, 111 (1878). See also This JOURNAL, **26**, 55 (1901).

[3] This JOURNAL, **26**, 55 (1901).

The triiodbenzol was converted into triioddinitrobenzol by boiling 5 grams of it with 140 cc. of a mixture of 4 parts of fuming nitric acid (sp. gr. 1.5) and 1 part of common strong nitric acid for half an hour. The mixture, on cooling, deposited yellowish-white crystals, which were purified by crystallization from a mixture of benzol and ligroin.

Action of Sodic Methylate on Triioddinitrobenzol.

A preliminary experiment showed that sodic methylate in methyl alcoholic solution had but slight action in the cold, the solution being only light-yellow even after long standing, and the crude product melting at 195° to 200°. Accordingly, we carried on the reaction hot, as follows: Fifteen grams of triioddinitrobenzol were dissolved in 150 cc. of absolute methyl alcohol and mixed with a solution of sodic methylate made by treating 1.9 grams of sodium with methyl alcohol. This gives 3 molecules of sodic methylate for each molecule of the triioddinitrobenzol. The mixture was gently boiled for about eight hours in a flask with a return-condenser. It took on a brownish-yellow color almost at once, and this color did not alter as the reaction continued. The solvent was allowed to evaporate spontaneously at the end of the heating and the liquid poured off from the crystals after about half of it had evaporated. The residue left by the evaporation of the second half of the solvent, was washed thoroughly with water. The washings had a red color, indicating probably the salt of a phenol. The residue, insoluble in water, was crystallized from alcohol, when light-yellow clumps of radiating needles were obtained mixed with amorphous particles. The needles were separated mechanically and recrystallized from alcohol until they showed the constant melting-point 128°, when they were dried at 100° and analyzed with the following result:

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[1] This Journal, **26**, 58 (1901).

I. 0.1621 gram substance gave, on combustion, 0.0920 gram CO_2 and 0.0219 gram H_2O.

II. 0.1362 gram substance gave, by the Carius method, 0.1818 gram AgI.

III. 0.2338 gram substance gave 0.3135 gram AgI.

	Calculated for $C_6HI_3NO_2OCH_3$.	Found. I.	II.	III.
C	15.82	15.48	....	....
H	0.75	1.50	....	....
I	71.73	....	72.16	72.46

The substance is therefore the triiodnitroanisol.

Properties of the Triiodnitroanisol, $C_6HI_3NO_2OCH_3$.—Crystallized from alcohol, it forms white or very light-yellow, slender prisms, terminated by a single plane at an oblique angle. It melts at 128°. It is freely soluble in benzol, ether, toluol, chloroform, acetone, or carbonic disulphide; moderately soluble in cold ethyl or methyl alcohol, freely soluble when hot; somewhat soluble in cold, more soluble in hot glacial acetic acid; insoluble in ligroin or water. Strong sulphuric acid dissolves it, giving a yellow solution; strong hydrochloric acid, or nitric acid, or sodic hydrate has no apparent action.

The less soluble portion of the product from the action of sodic methylate on triioddinitrobenzol yielded, after washing, recrystallization from alcohol, mechanical separation, and frequent recrystallizations from alcohol, a crystalline substance which melted between 253° and 256°. Unfortunately, the amount was too small to allow us to purify this body thoroughly, but an analysis of our best specimen gave the following results:

0.1635 gram substance gave, by the Carius method, 0.1122 gram AgI.

	Calculated for $C_6HI(OCH_3)_3NO_2$.	Found.
I	37.47	37.10

This analysis indicates that the substance was formed by the replacement of 2 atoms of iodine by methoxy groups in the triiodnitroanisol, which we have shown was a principal product of the reaction. This single analysis of a substance not certainly pure obviously needs confirmation before it can be accepted.

Action of Sodic Ethylate on Triioddinitrobenzol.

Ten grams of triioddinitrobenzol, dissolved in 75 cc. of absolute alcohol, were mixed with a solution of sodic ethylate prepared from 1.3 grams of sodium; that is, 3 molecules of ethylate were used to each molecule of the substituted benzol. A slight reaction took place in the cold, as shown by the appearance of a brownish-red color, but disregarding this, the mixture was boiled for fifteen minutes in a flask with a return-condenser. The dark-red solution was allowed to evaporate spontaneously, and the residue washed with water. The light-colored insoluble portion was recrystallized from alcohol until it showed the constant melting-point 130°, when it was dried at 100° and analyzed with the following result. It contained no iodine:

0.1382 gram substance gave, on combustion, 0.2365 gram CO_2 and 0.0627 gram H_2O.

	Calculated for $C_6H_2(NO_2)_2(OC_2H_5)_2$.	Found.
C	46.88	46.68
H	4.69	5.05

This proves that the substance is a dinitroresorcine diethyl ether, and we think it identical with that discovered by Warren and one of us,[1] although it melts at 130°, and the melting-point given in the paper cited is 133°. We explain this difference in melting-point by assuming the presence of an obstinately adhering impurity in our substance.

A small quantity of another body was also observed crystallizing in plates and melting near 200°, but we could not obtain enough of it for purification.

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[1] This JOURNAL, **13**, 170 (1891).

Action of Sodic Malonic Ester on Triioddinitrobenzol.

A number of different products were obtained from this reaction. Twenty-five grams of triioddinitrobenzol were dissolved in 300 cc. of absolute alcohol and mixed with 22 grams of malonic ester previously treated with the sodic ethylate made from 3.2 grams of sodium and 100 cc. of absolute alcohol. A red color appeared at once, but disregarding this, the mixture was boiled for five minutes in a flask with a return-condenser, and the product was then allowed to evaporate spontaneously. The residue was much less oily if the liquid had been acidified with hydrochloric acid, but in that case the salt of the substituted malonic ester could not be washed out directly with water, and the later purification was therefore more difficult. The residue was washed with water, and the portion insoluble in water, which was the principal product of the reaction, was washed several times with warm alcohol, which formed a dark-green solution and left a mass of yellow crystals. These were purified by crystallization from alcohol containing a little benzol until they showed the constant melting-point 160°, when they were dried at 100° and analyzed with the following result:

I. 0.2203 gram substance gave, on combustion, 0.1440 gram CO_2 and 0.0189 gram H_2O.

II. 0.2364 gram substance gave, by the Carius method, 0.2649 gram AgI.

III. 0.1781 gram substance gave 0.1991 gram AgI.

	Calculated for $C_6H_2I_2(NO_2)_2$.	Found.		
		I.	II.	III.
C	17.15	17.83	....	....
H	0.47	0.96	....	....
I	60.47	....	60.57	60.43

The substance is therefore a diioddinitrobenzol formed from the triioddinitrobenzol by the replacement of 1 atom of iodine by 1 of hydrogen. To judge from the melting-point 160°, it is the same as the diioddinitrobenzol prepared by Istrati and Georgescu[1] by the action of nitric acid on their triiodbenzol melting at 83° to 84° (probably the vicinal isomer), since their dinitro body melts at 160° to 162°.

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[1] Buletinul Soc. Sci. Fiz. Bucuresci, **1**, 63.

Properties of Diioddinitrobenzol, $C_6H_2I_2(NO_2)_2$.—Crystallized from benzol containing a little alcohol it formed usually square-ended prisms arranged in groups formed by the union of the long sides of the prisms, so that the ends look like flights of steps. Less often it occurs in prisms terminated by several planes belonging apparently to the monoclinic system. From alcohol it crystallizes in long, slender needles very much branched, forming irregular, feather-like forms. It has a full yellow color and melts at 160°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; moderately soluble in cold ethyl or methyl alcohol, more so when hot; very slightly soluble in ligroin; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong sulphuric acid dissolves it slightly with a faint yellow color, but it seems to be unaffected by strong hydrochloric acid or nitric acid, or an aqueous solution of sodic hydrate.

Ioddinitrophenylmalonic Ester, $C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$.

In the preparation of the diioddinitrobenzol it was mentioned that the product insoluble in water was washed with warm alcohol. The dark-green washings, when allowed to evaporate spontaneously, left a mixture of white and yellow crystals. The latter were picked out mechanically as far as possible, and then recrystallized from ligroin until they showed the constant melting-point 83°, when they were dried *in vacuo* and analyzed with the following result:

I. 0.1821 gram substance gave, by the Carius method, 0.0946 gram AgI.

II. 0.1696 gram substance gave 0.0899 gram AgI.

	Calculated for $C_6H_2I(NO_2)_2CH(COOC_2H_5)_2$.	Found. I.	Found. II.
I.	28.07	28.08	28.67

The substance is therefore ioddinitrophenylmalonic ester, formed by the replacement of 1 atom of iodine by the malonic ester radical and of a second by hydrogen.

Properties of Ioddinitrophenylmalonic Ester.—It crystallizes from alcohol in well-developed yellow, rhombic plates with each acute angle truncated by a plane, which look as if they belonged to the orthorhombic system. It melts at 83°, and is freely soluble in alcohol, ether, benzol, methyl alcohol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; moderately soluble in ligroin; insoluble in water. Ligroin is the best solvent for it. Strong hydrochloric acid has no apparent action on it. Strong nitric acid or sulphuric acid dissolves it, giving a yellow solution. Sodic hydrate gives with it a red solution of the sodium salt. In this respect it resembles most of the other nitrophenylmalonic esters known.

The colorless crystals which were mixed with the ioddinitrophenylmalonic ester, when first obtained, were found also in the mother-liquors from its recrystallization. They melted at about 73° and contained no iodine, but were not obtained in sufficient quantity for identification.

Addition-Compound of Diioddinitrobenzol and Triioddinitrobenzol, $[C_6H_2I_2(NO_2)_2]_2C_6I_3(NO_2)_2$.

In some of the experiments on the action of sodic malonic ester on triioddinitrobenzol still another compound was obtained, which was less soluble in cold alcohol even than the diioddinitrobenzol. It appeared in largest amount in the products of one reaction, which was carried on at ordinary temperatures. It was purified by repeated crystallization from hot alcohol, but we found it very hard to get it absolutely pure, as is shown by the following analyses of the substance dried at 100°:

I. 0.2660 gram substance gave, by the Carius method, 0.3119 gram AgI.

II. 0.2488 gram substance gave 0.2918 gram AgI.

	Calculated for	Found.	
	$[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2$.	I.	II.
I	64.14	63.37	63.40

These analyses indicate that the substance is an addition-compound of 2 molecules of the diioddinitrobenzol and 1 of the triioddinitrobenzol, but they are obviously insufficient to establish its nature with certainty. The proof of its composition was given by its decomposition into its components and its synthesis from them. By crystallizing the substance from a mixture of alcohol and benzol, it was in time broken up into diioddinitrobenzol, melting at 160°, and triioddinitrobenzol, melting at 210°. These products were also recognized by their crystalline forms. Alcohol alone does not bring about this decomposition. To achieve its synthesis, a mixture of diioddinitrobenzol with triioddinitrobenzol, in the proportion of 2 molecules of the former to 1 of the latter, was boiled for two hours with alcohol in a flask with a return-condenser. Upon allowing the solids to crystallize two sorts of crystals were obtained, square-ended prisms like the addition-compound and needles like those of the diioddinitrobenzol, when crystallized from alcohol. The mother-liquors containing the needles were heated with a small additional amount of the triioddinitrobenzol, and after three recrystallizations a product was obtained which melted between 181° and 184°, and was identical in color and crystalline form with our addition-product. There can be no doubt, therefore, that our substance is really the compound

$$[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2.$$

That it is not a mixture of the two components was shown by the fact that it gave, when crystallized from alcohol, crystals of only one sort, which differed from those of either of its components.

Properties of the Addition-Compound $[C_6H_2I_2(NO_2)_2]_2C_6HI_3(NO_2)_2$.—It crystallizes from alcohol in long, slender, square-ended prisms of a paler yellow than those of the diioddinitrobenzol, entirely different on the one hand from the long, slender, branching needles of the diioddinitrobenzol, and on the other from the thick needles in radiating bunches of the triioddinitrobenzol. It melts at 182° and is freely soluble in methyl alcohol, benzol, ether, chloroform, acetone, or carbonic disulphide; slightly soluble in cold, soluble in hot alcohol (difference from diioddinitrobenzol); slightly soluble in cold glacial acetic acid, freely soluble when hot; slightly soluble in ligroin whether cold or hot. Alcohol is the best solvent for it. Benzol, even when mixed with alcohol, breaks it up into its components. It is not perceptibly affected by the three strong acids or an aqueous solution of sodic hydrate.

THE EXISTENCE OF HYDRATES IN SOLUTIONS OF CERTAIN NON-ELECTROLYTES AND THE NON-EXISTENCE OF HYDRATES IN SOLUTIONS OF ORGANIC ACIDS.

BY HARRY C. JONES AND FREDERICK H. GETMAN[1] (CARNEGIE RESEARCH ASSISTANT).

Having found that electrolytes in general form hydrates of greater or less complexity with water,[2] we naturally turned our attention to the non-electrolytes. These have been studied by the same general methods as were employed with the electrolytes, the conductivity method, of course, not being used.

In determining the freezing-point of dilute solutions, an ordinary Beckmann thermometer was used. For the more concentrated solutions, Beckmann thermometers having a range of 12° and 25° were employed. An alcohol thermometer was used to measure the freezing-points of the most concentrated solutions. The freezing-mixtures employed were salt and ice, calcium chloride and ice, or solid carbon dioxide and alcohol, depending on the concentration of the solution whose freezing-point was to be determined.

For the method of determining, from the experimental data, whether or not hydrates exist in solution, reference must be made to one of our earlier papers.[3] The specific gravities of the solutions were determined and used in the calculation of the composition of the hydrates in solution in a manner strictly analogous to that employed with the electrolytes.

In the following tables of "freezing-point measurements" *m* is the concentration in terms of gram-molecular normal, Δ

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[1] This investigation was made possible by a grant from the Carnegie Institution, with which Dr. Getman was appointed a Research Assistant.

[2] Ztschr. phys. Chem., 46, 244; Phys. Rev., 18, 146; This JOURNAL, 31, 303.

[3] *Loc. cit.*

is the lowering of the freezing-point observed; and $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the tables of "specific gravities," m is the concentration in terms of gram-molecular normal, $W_{\text{Sol.}}$ is the weight of 25 cc. of the solution; $W_{\text{substance}}$ is the weight of the substance in question in 25 cc. of the solution; W_{H_2O} is the weight of water in 25 cc. of the solution; and *correction* is the percentage difference between the amount of water in 1 liter of the solution and 1,000 grams of water.

In the tables of "hydrates," m is the concentration in terms of gram-molecular normal; L the calculated molecular lowering for non-electrolytes; $\frac{\Delta}{m}$ the observed molecular lowering; L′ the molecular lowering corrected for specific gravities; m the number of gram-molecules of water combined with the substance at the concentration expressed by the abscissæ; $H = \frac{m}{m'}$ is the number of molecules of water combined with 1 molecule of the substance at the concentration in question.

We have worked with thirteen non-electrolytes, and the results obtained are given in the following tables. Care was taken in every case to test the purity of the substance used, and to purify the compound when the specimen, furnished in most cases by Kahlbaum, was not sufficiently pure.

Methyl Alcohol.

The results are given in Tables I. to III. A glance at Table I. will show a marked increase in the molecular lowering, $\frac{\Delta}{m}$, with increase in concentration. This would suggest at first sight that there is considerable hydration in the more concentrated solutions. Such, however, is not the case. When the observed molecular lowering is corrected for specific gravity, *i. e*, referred to 1,000 grams of the solvent, the observed lowering does not differ greatly from the calculated. This is seen by comparing column L′ with column L, Table III. At no concentration do we find as much as 1 molecule of water combined with every molecule of the alcohol.

The freezing-point data for methyl alcohol are plotted as a curve (Fig. I.). The abscissæ represent concentrations and the ordinates molecular lowering of the freezing-point.

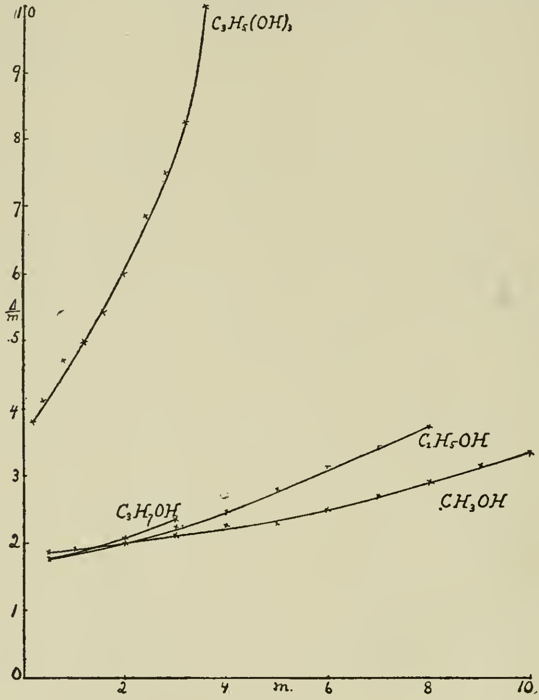

Fig. I.

Table I.—Freezing-point Measurements.

Methyl alcohol, $CH_4O = 32.04$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.935	1.87
1.0	1.898	1.90
2.0	....	....
3.0	6.440	2.15
4.0	9.130	2.28
5.0	11.500	2.30
6.0	15.000	2.50
7.0	19.000	2.71
8.0	23.500	2.94
9.0	28.500	3.17
10.0	33.500	3.35

Table II.—Specific Gravities.

m.	$W_{Sol.}$	W_{CH_4O}.	W_{H_2O}.	Correction. Per cent.
0.5	24.8825	0.4000	24.4825	2.07
1.0	24.8071	0.8000	24.0071	3.97
2.0	24.7032	1.6000	23.1032	7.89
3.0	24.5111	2.4000	22.1111	11.86
4.0	24.3773	3.2000	21.1773	15.29
5.0	24.2655	4.0000	20.2655	18.94
6.0	24.1013	4.8000	19.3013	22.79
7.0	24.0195	5.6000	18.4195	26.32
8.0	23.8966	6.4000	17.4966	30.01
9.0	23.7476	7.2000	16.5476	33.81
10.0	23.6050	8.0000	15.6050	37.58

Table III.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.	m.	H.
0.5	1.86	1.87	1.83	..	..
1.0	1.86	1.90	1.86	..	..
..	....	....	....	..	..
3.0	1.86	2.15	1.90	1.1	0.4
4.0	1.86	2.28	1.93	2.0	0.5
5.0	1.86	2.30	1.87	..	..
6.0	1.86	2.50	1.93	2.0	0.3
7.0	1.86	2.71	2.00	3.9	0.5
8.0	1.86	2.94	2.06	5.4	0.7
9.0	1.86	3.17	2.10	6.4	0.7
10.0	1.86	3.35	2.10	6.4	0.6

Ethyl Alcohol.

Results were obtained with ethyl alcohol which are of the same general character as those given by methyl alcohol. The freezing-points of the solutions of ethyl alcohol are, however, lower than those of methyl alcohol of the same concentrations. The corrections for specific gravities are larger for the ethyl alcohol, so that the amount of hydration shown by this substance is not very much greater than that shown by methyl alcohol.

The data for ethyl alcohol are recorded in Tables IV. to VI., and the freezing-point measurements are plotted in Fig. I. The magnitude of the hydration shown by ethyl alcohol is seen in Table VI. There is, of course, the possibility that ethyl alcohol undergoes some polymerization in solution and that the true hydration is greater than would be indicated by these figures.

Table IV.—Freezing-point Measurements.

Ethyl alcohol, $C_2H_6O = 46.06$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.895	1.790
1.0	1.872	1.872
2.0	4.010	2.005
3.0	6.720	2.240
4.0	9.960	2.490
5.0	14.200	2.840
6.0	19.000	3.160
7.0	24.250	3.460
8.0	30.000	3.740

Table V.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_2H_6O}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8275	0.5750	24.2525	2.99
1.0	24.7147	1.1500	23.5647	5.74
2.0	24.5514	2.3100	22.2414	9.03
3.0	24.3845	3.4500	20.9345	16.26
4.0	24.2400	4.6200	19.6200	21.52
5.0	24.0891	5.7500	18.3391	26.65
6.0	23.8720	6.9000	16.9720	32.11
7.0	23.6930	8.0500	15.6430	37.43
8.0	23.4333	9.2400	14.1933	43.23

Table VI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.	m.	H.
0.5	1.86	1.790	1.740	..	..
1.0	1.86	1.872	1.765	..	..
2.0	1.86	2.005	1.825	..	..
3.0	1.86	2.240	1.873	..	..
4.0	1.86	2.490	1.955	2.7	0.7
5.0	1.86	2.840	2.082	6.0	1.2
6.0	1.86	3.160	2.150	6.9	1.1
7.0	1.86	3.460	2.166	7.8	1.1
8.0	1.86	3.740	2.120	6.8	0.8

n-Propyl Alcohol.

Propyl alcohol gives lowerings of the freezing-point that differ markedly from those produced by methyl and ethyl alcohols. The molecular lowering increases with the concentration up to a certain point, passes through a maximum and then decreases (Table VII.). The corrected molecular lowering is smaller than the theoretical value, 1.86, at nearly all concentrations, and becomes very much smaller in the more concentrated solutions. Indeed, in a six-normal solution the corrected molecular lowering becomes less than half of the theoretical value. This is shown in Table IX.

The explanation of these results is to be found, undoubtedly, in the polymerization of the molecules of normal propyl alcohol, especially in concentrated solution. It is, therefore, impossible to say in such cases whether or not there is any hydration.

Table VII.—Freezing-point Measurements.

n-Propyl alcohol, C_3H_7OH.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.890	1.78
1.0	1.900	1.90
2.0	4.160	2.08
3.0	7.100	2.37
4.0	8.820	2.20
5.0	9.450	1.89

Table VIII.—Specific Gravities.

m.	$W_{\text{Sol.}}$	$W_{C_3H_7OH}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8348	0.7500	24.0848	3.66
1.0	24.6690	1.5000	23.1690	7.32
2.0	24.4770	3.0000	21.4770	14.09
3.0	24.2478	4.5000	19.7478	21.0
4.0	23.9394	6.0000	17.9394	28.24
5.0	23.5960	7.5000	16.0960	33.62
6.0	23.2411	9.0000	14.2411	43.04
7.0	22.8372	10.5000	12.3372	50.65

Table IX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.5	1.86	1.78	1.71
1.0	1.86	1.90	1.76
2.0	1.86	2.08	1.79
3.0	1.86	2.37	2.04
4.0	1.86	2.20	1.58
5.0	1.86	1.89	1.25
6.0	1.86	1.50	0.85

Acetone.

The freezing-point lowerings produced by acetone increase considerably with increase in the concentration of the solution, but the correction for specific gravity is unusually large (Table XI.). When the proper corrections are applied, the "true molecular lowerings" decrease with increase in the

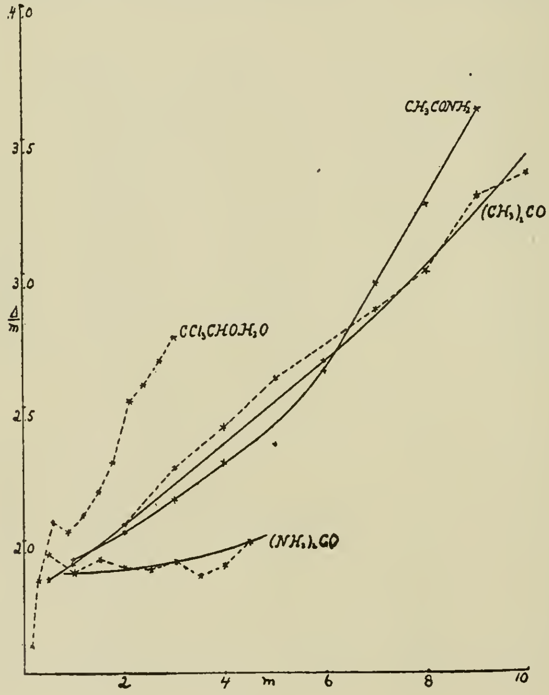

Fig. II.

concentration of the solutions. The experimental values at all concentrations studied are below the calculated value for a non-dissociated, non-polymerized substance, and at great concentrations the values found fall very much below the theoretical value (column L′, Table XII.).

This shows that the acetone undergoes polymerization in such solutions, the amount of the polymerization being a function of the concentration—increasing from the most dilute to the most concentrated solutions studied. The freezing-point curve is plotted in Fig. II.

Table X.—Freezing-point Measurements.

Acetone, $CH_3.CO.CH_3 = 58.06$.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.930	1.860
1.0	1.919	1.919
2.0	4.110	2.055
3.0	6.800	2.270
4.0	9.700	2.420
5.0	13.000	2.600
6.0	16.000	2.670
7.0	20.000	2.86
8.0	24.000	3.00
9.0	29.560	3.28
10.0	33.75	3.37

Table XI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_3H_6O}$.	W_{H_2O}.	Correction. Per cent.
0.5	24.8177	0.7250	24.0927	3.63
1.0	24.7292	1.4500	23.2792	6.88
2.0	24.5396	2.9000	21.6396	13.44
3.0	24.3129	4.3500	19.9629	20.15
4.0	24.1056	5.8000	18.3056	26.78
5.0	23.8278	7.2500	16.5778	33.69
6.0	23.5748	8.7000	14.8748	40.00
7.0	23.2513	10.1500	13.1013	47.59
8.0	22.9160	11.6000	11.3160	54.74
9.0	22.5212	13.0500	9.4712	62.12
10.0	22.0880	14.5000	7.4880	70.04

Table XII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.5	1.86	1.860	1.790
1.0	1.86	1.919	1.787
2.0	1.86	2.055	1.780
3.0	1.86	2.270	1.816
4.0	1.86	2.420	1.774
5.0	1.86	2.600	1.724
6.0	1.86	2.670	1.586
7.0	1.86	2.860	1.499
8.0	1.86	3.000	1.358
9.0	1.86	3.280	1.246
10.0	1.86	3.370	1.011

Acetamide.

While the value of $\frac{\Delta}{m}$ for acetamide increases rapidly with the concentration, the corrected molecular lowering, L′, Table XV., does not change appreciably in magnitude. Indeed, the values found at the various dilutions do not differ appreciably from the theoretical value 1.86. This indicates that acetamide neither forms hydrates nor undergoes polymerization at any dilution.

There is, of course, the possibility that these influences are simultaneously operative, but in order that this should be true, we would have to assume that the magnitude of each of these influences was exactly equal at all concentrations, which is a highly improbable assumption. The freezing-point data for acetamide are plotted in Fig. II.

Table XIII.—Freezing-point Measurements.

Acetamide, $CH_3.CO.NH_2$ = 59.09.

m.	Δ.	$\frac{\Delta}{m}$.
0.4	0.782	1.93
1.0	1.930	1.93
2.0	4.050	2.03
3.0	6.440	2.15
4.0	9.150	2.29
5.0	11.800	2.36
6.0	15.800	2.63
7.0	20.750	2.96
8.0	26.000	3.25
9.0	32.500	3.61

Table XIV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{CH_3CONH_2}$.	W_{H_2O}.	Correction. Per cent.
0.4	24.9502	0.5900	24.3602	2.56
1.0	25.0486	1.4750	23.5736	5.70
2.0	25.1446	2.9500	22.1946	11.22
3.0	25.2355	4.4250	20.8105	16.76
4.0	25.3858	5.9000	19.4858	22.06
5.0	25.4530	7.3750	18.0780	27.69
6.0	25.5606	8.8500	16.7106	33.16
7.0	25.6660	9.3250	16.3410	34.64
8.0	25.7861	11.8000	13.9861	44.06
9.0	25.8257	13.2750	12.5500	49.80

Table XV.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.4	1.86	1.93	1.88
1.0	1.86	1.93	1.82
2.0	1.86	2.03	1.81
3.0	1.86	2.15	1.79
4.0	1.86	2.29	1.79
5.0	1.86	2.36	1.71
6.0	1.86	2.63	1.76
7.0	1.86	2.96	1.94
8.0	1.86	3.25	1.82
9.0	1.86	3.61	1.79

Urea.

The observed molecular depression produced by urea does not change appreciably with the concentration, as is seen in column $\frac{\Delta}{m}$, Table XVI. When these values are corrected for specific gravities, the true molecular lowerings decrease quite markedly with increase in the concentration of the solutions. This is seen in column L′, Table XVIII.

Here, again, we have considerable polymerization, and the amount of the polymerization increases with the concentration of the solutions.

The curve for urea is given in Fig. II.

Table XVI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.5	0.975	1.95
1.0	1.878	1.88
1.5	2.900	1.93
2.0	3.800	1.90
2.5	4.724	1.89
3.0	5.767	1.92
3.5	6.555	1.87
4.0	7.625	1.91
4.5	8.975	1.99

Table XVII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Urea.}$	$W_{H_2O.}$	Correction. Per cent.
0.5	25.1409	0.7500	24.3909	2.44
1.0	25.3258	1.5000	23.8258	4.70
1.5	25.4996	2.2500	23.2496	7.00
2.0	25.7206	3.0000	22.7206	9.12
2.5	25.8933	3.7500	22.1433	11.43
3.0	26.1085	4.5000	21.6085	13.57
3.5	26.2992	5.2500	21.0492	15.80
4.0	26.4785	6.0000	20.4785	18.09
4.5	26.6456	6.7500	19.8956	20.42

Table XVIII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.5	1.86	1.95	1.90
1.0	1.86	1.88	1.80
1.5	1.86	1.93	1.75
2.0	1.86	1.90	1.73
2.5	1.86	1.89	1.67
3.0	1.86	1.92	1.66
3.5	1.86	1.87	1.57
4.0	1.86	1.91	1.57
4.5	1.86	1.99	1.58

Chloral Hydrate.

The freezing-point curve for chloral hydrate (Fig. II.) is somewhat remarkable. It shows one or two well-defined breaks, the meaning of which is not apparent. While the observed molecular lowering increases quite markedly with the concentration (Table XIX.) the corrected molecular lowering, L′, Table XXI., shows only slight increase as the concentration of the solution increases. The true molecular lowering produced by chloral hydrate is never much larger than the theoretical value, and, therefore, this substance does not show any marked hydration at any of the dilutions with which we worked.

Table XIX.—Freezing-point Measurements.

Chloral hydrate, $CCl_3.COH.H_2O = 165.38$.

m.	Δ.	$\frac{\Delta}{m}$.
0.15	0.260	1.73
0.30	0.556	1.85
0.60	1.241	2.07
0.90	1.825	2.03
1.2	2.505	2.09
1.5	3.274	2.18
1.8	4.176	2.29
2.1	5.200	2.52
2.4	6.170	2.58
2.7	7.200	2.67
3.0	8.280	2.76

Table XX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{CCl_3.COH.H_2O}$.	W_{H_2O}.	Correction. Per cent.
0.15	25.2450	0.6202	24.6248	1.50
0.3	25.5002	1.2405	24.2597	2.96
0.6	26.0785	2.4810	23.5975	5.61
0.9	26.5458	3.7215	22.8243	8.70
1.2	27.1197	4.9620	22.1577	11.37
1.5	27.6235	6.1025	21.5210	13.92
1.8	28.1998	7.4430	20.7568	16.97
2.1	28.7492	8.6835	20.0657	19.74
2.4	29.1582	9.9240	19.2342	23.06
2.7	29.3230	11.1645	18.1585	27.37
3.0	30.2896	12.4050	17.8846	28.46

Table XXI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.15	1.86	1.73	1.70
0.3	1.86	1.85	1.80
0.6	1.86	2.07	1.95
0.9	1.86	2.03	1.85
1.2	1.86	2.09	1.86
1.5	1.86	2.18	1.88
1.8	1.86	2.29	1.90
2.1	1.86	2.52	2.02
2.4	1.86	2.58	2.00
2.7	1.86	2.67	1.95
3.0	1.86	2.76	1.97

Glycerol.

The case of glycerol among the non-electrolytes is particularly interesting, in that it shows very marked hydration. This would be indicated by the large molecular lowerings recorded in Table XXII., and curve Fig. I., and is obvious from the large values of the corrected molecular lowerings, L′, in Table XXIV.

The degree of the hydration is shown in column H, Table XXIV. We are impressed, first, by the large number of molecules of water combined with 1 molecule of the glycerol, and, second, by the fact that the complexity of the hydrate increases regularly from the most dilute to the most concentrated solution investigated. The hydrate curve for glycerol is given in Fig. IV., where the abscissae represent concentrations and the ordinates the number of molecules of water combined with 1 molecule of glycerol.

Table XXII.—Freezing-point Measurements.

Glycerol, $C_3H_5(OH)_3 = 92.08$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.76	3.80
0.4	1.65	4.12
0.8	3.75	4.70
1.2	6.00	5.00
1.6	8.70	5.44
2.0	12.00	6.00
2.4	16.50	6.87
2.8	21.00	7.50
3.2	26.50	8.28
3.6	36.00	10.00

Table XXIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_3H_5(OH)_3}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2010	0.4600	24.7410	1.04
0.4	25.3351	0.9200	24.4151	2.34
0.8	25.8055	1.8400	23.9655	4.14
1.2	26.2256	2.7600	23.4656	6.14
1.6	26.6665	3.6800	22.9865	8.05
2.0	27.0463	4.6000	22.4463	10.21
2.4	27.4440	5.5200	21.9240	12.30
2.8	27.8344	6.4400	21.3944	14.42
3.2	28.1801	7.3600	20.8201	16.72
2.6	28.5580	8.2800	20.2780	18.89

Table XXIV.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.2	1.86	3.80	3.76	28.0	140.0
0.4	1.86	4.12	4.03	30.1	75.2
0.8	1.86	4.70	4.51	32.6	40.8
1.2	1.86	5.00	4.70	33.5	28.0
1.6	1.86	5.44	5.00	34.9	21.8
2.0	1.86	6.00	5.40	36.4	18.2
2.4	1.86	6.87	6.03	38.6	16.1
2.8	1.86	7.50	6.42	39.4	10.5
3.2	1.86	8.28	7.30	41.4	12.9
3.6	1.86	10.00	8.11	42.8	11.9

Glucose.

Turning to the carbohydrates, we find very little hydration shown by glucose. The freezing-point lowerings produced by glucose are plotted in Fig. III. A comparison of the corrected molecular lowerings, L′, Table XXVII., with the theoretical molecular lowering, L, of the same table, will show that in the more concentrated solutions the experimental value is slightly greater than the theoretical. The difference is so small that the amount of hydration shown by this substance is very slight indeed.

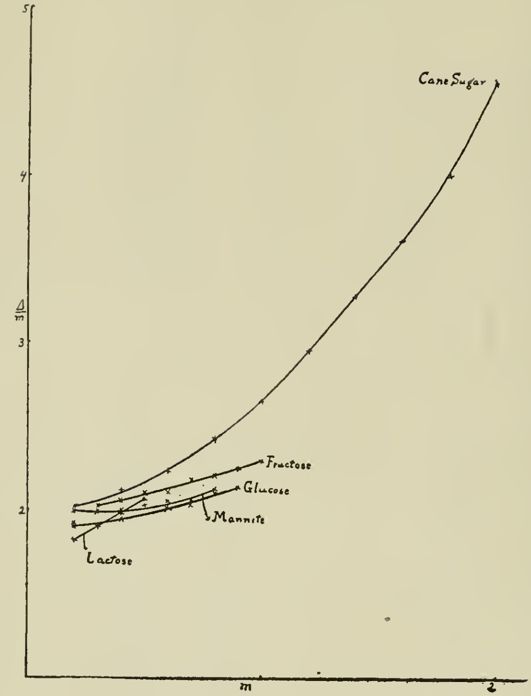

Fig. III.

Table XXV.—Freezing-point Measurements.

Glucose, $C_6H_{12}O_6 = 180$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.380	1.91
0.3	0.574	1.91
0.4	0.780	1.95
0.5	1.023	2.04
0.6	1.220	2.03
0.7	1.430	2.04
0.8	1.690	2.11
0.9	1.930	2.14

Table XXVI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{12}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2810	0.9000	24.3810	2.48
0.3	25.4412	1.3500	24.0912	3.64
0.4	25.6245	1.8000	23.8245	4.70
0.5	25.8192	2.2500	23.5689	5.72
0.6	25.9539	2.7000	23.2539	6.98
0.7	26.1361	3.1500	22.9861	8.06
0.8	26.2819	3.6000	22.6819	9.27
0.9	26.4712	4.0500	22.4212	10.32
1.0	26.5827	4.5000	22.0827	11.67

Table XXVII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.2	1.86	1.91	1.86
0.3	1.86	1.91	1.85
0.4	1.86	1.95	1.86
0.5	1.86	2.04	1.92
0.6	1.86	2.03	1.89
0.7	1.86	2.04	1.88
0.8	1.86	2.11	1.91
0.9	1.86	2.14	1.93

Fructose.

Fructose, unlike glucose, shows considerable hydration, especially in the more dilute solutions. The complexity of the hydrates is seen in column H, Table XXX. Fructose, like glycerol, forms hydrates which are more and more complex the more dilute the solution. The non-electrolytes that form hydrates in solution thus differ from those of the electrolytes. The complexity of the latter reaches a maximum at a definite concentration and then becomes less and less, both with increase in the dilution and with increase in the concentration of the solutions. This is probably connected in some way with the fact that with the non-electrolytes we have only molecules present, while in solutions of electrolytes we have both molecules and ions present. The curve of hydrates for fructose is given in Fig. IV.

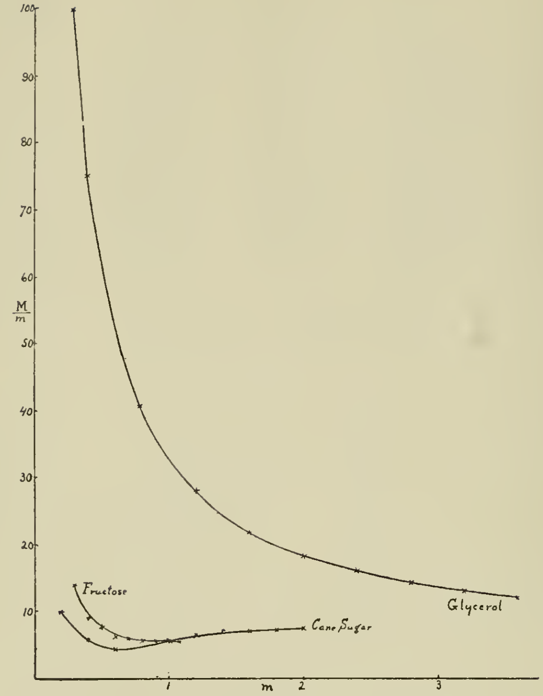

Fig. IV.

Table XXVIII.—Freezing-point Measurements.

Fructose, $C_6H_{12}O_6 = 180$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.384	1.92
0.3	0.610	2.03
0.4	0.830	2.07
0.5	1.054	2.11
0.6	1.265	2.11
0.7	1.535	2.19
0.8	1.765	2.21
0.9	2.033	2.26
1.0	2.300	2.30

Table XXIX.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{12}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.3519	0.9000	24.4519	2.19
0.3	25.5315	1.3500	24.1815	3.27
0.4	25.7306	1.8000	23.9306	4.28
0.5	25.8911	2.2500	23.6411	5.44
0.6	26.0845	2.7000	23.3845	6.46
0.7	26.1856	3.1500	23.0356	7.86
0.8	26.4080	3.6000	22.8080	8.77
0.9	26.5790	4.0500	22.5290	8.88
1.0	26.7699	4.5000	22.2699	10.92

Table XXX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.2	1.86	1.92	1.88	..	...
0.3	1.86	2.03	1.96	2.8	14.0
0.4	1.86	2.07	1.98	3.7	9.2
0.5	1.86	2.11	2.00	3.9	7.8
0.6	1.86	2.11	1.99	3.6	6.0
0.7	1.86	2.19	2.02	4.4	6.3
0.8	1.86	2.21	2.02	4.4	5.5
0.9	1.86	2.26	2.04	5.0	5.5
1.0	1.86	2.30	2.05	5.3	5.3

Mannite.

Mannite, on the other hand, has very little power to combine with water at any of the dilutions at which work could be done. On account of its comparatively slight solubility, however, we could not work at any considerable concentration.

A comparison of column L′ with column L, Table XXXIII., shows that this substance gives molecular lowerings of the freezing-point of water that are only slightly greater than the theorerical lowering. Further, there is no apparent regularity in the difference between the value found and the calculated value. The amount of hydration is so slight that it was not even calculated. The values of $\frac{\Delta}{m}$, Table XXXI., for this substance are plotted in Fig. III.

Table XXXI.—Freezing-point Measurements.

Mannite, $C_6H_{10}O_6 = 182$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.400	2.00
0.3	0.600	2.00
0.4	0.800	2.00
0.5	1.033	2.07
0.6	1.234	2.06
0.7	1.440	2.06
0.8	1.700	2.13

Table XXXII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_6H_{14}O_6}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.2628	0.9100	24.3528	2.59
0.3	25.4320	1.3650	24.0670	3.73
0.4	25.5747	1.8200	23.7547	4.98
0.5	25.7431	2.2750	23.4681	6.13
0.6	25.9235	2.7300	23.1935	7.23
0.7	26.0495	3.2350	22.8145	8.74
0.8	26.1478	3.6400	22.5078	9.97

Table XXXIII.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L′.
0.2	1.86	2.00	1.95
0.3	1.86	2.00	1.93
0.4	1.86	2.00	1.90
0.5	1.86	2.07	1.95
0.6	1.86	2.06	1.91
0.7	1.86	2.06	1.88
0.8	1.86	2.13	1.92

Lactose.

Lactose not only shows no hydration, but the corrected molecular lowerings, L′, Table XXXVI., are less than the theoretical value 1.86. This would indicate a certain amount of polymerization in the solutions. On account of the limited solubility of lactose we could not study concentrations greater than half-normal.

The molecular lowerings $\frac{\Delta}{m}$, Table XXXIV., found for lactose are plotted in a curve, Fig. III.

Table XXXIV.—Freezing-point Measurements.

Lactose, $C_{12}H_{22}O_{11} = 342.22$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.364	1.82
0.3	0.574	1.91
0.4	0.792	1.98
0.5	1.030	2.06

Table XXXV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_{12}H_{22}O_{11}}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.5793	1.7100	23.8693	4.52
0.3	25.8796	2.5650	23.3146	6.74
0.4	26.1958	3.4200	22.7758	8.89
0.5	26.5176	4.2750	22.2426	11.03

Table XXXVI.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.
0.2	1.86	1.82	1.74
0.3	1.86	1.91	1.78
0.4	1.86	1.98	1.80
0.5	1.86	2.06	1.83

Cane-Sugar.

It has been known for some time that cane-sugar, in concentrated solutions, gives molecular lowerings that are considerably greater than the theoretical value. Arrhenius[1] established this fact in connection with his early work on the theory of electrolytic dissociation. We determined to make a comparatively thorough study of cane-sugar, using solutions much more concentrated than those employed by Arrhenius. We found that we could work to a concentration of twice normal. The freezing-point lowerings given in Table XXXVII. are plotted in Fig. III.

Cane-sugar shows very considerable hydration. The curve showing the complexity of the hydrates of cane-sugar is given in Fig. IV.

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[1] Ztschr. phys. Chem., 2, 495 (1888).

Table XXXVII.—Freezing-point Measurements.

Cane-Sugar, $C_{12}H_{22}O_{11}$.

m.	Δ.	$\frac{\Delta}{m}$.
0.2	0.404	2.02
0.4	0.848	2.12
0.6	1.345	2.24
0.8	1.950	2.44
1.0	2.662	2.66
1.2	3.550	2.96
1.4	4.612	3.29
1.6	5.800	3.62
1.8	7.230	4.02
2.0	9.130	4.57

Table XXXVIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{C_{12}H_{22}O_{11}}$.	W_{H_2O}.	Correction. Per cent.
0.2	25.5904	1.7100	23.8804	4.48
0.4	26.2388	3.4200	22.8188	8.72
0.6	26.8635	5.1300	21.7335	13.06
0.8	27.5078	6.8400	20.6678	17.33
1.0	28.0680	8.5500	19.5180	21.93
1.2	28.6920	10.2600	18.4320	26.27
1.4	29.3441	11.9700	17.3741	30.50
1.6	29.8762	13.6800	16.1962	35.22
1.8	30.4824	15.3900	15.0924	39.63
2.0	31.1005	17.1000	14.0005	44.0

Table XXXIX.—Hydrates.

m.	L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.2	1.86	2.02	1.93	2.0	10.0
0.4	1.86	2.12	1.94	2.3	5.8
0.6	1.86	2.24	1.95	2.5	4.2
0.8	1.86	2.44	2.02	4.4	5.5
1.0	1.86	2.66	2.07	5.5	5.5
1.2	1.86	2.96	2.18	8.1	6.7
1.4	1.86	3.29	2.29	10.4	7.4
1.6	1.86	3.62	2.35	11.6	7.2
1.8	1.86	4.02	2.43	13.0	7.2
2.0	1.86	4.57	2.56	15.2	7.6

Organic Acids.

The organic acids really belong in the class of the electrolytes. But since they are, generally speaking, weakly dissociated compounds, they have been studied as a class by themselves. Some of these substances contain a small amount of water of crystallization, but, generally, they crystallize either without water or with only a small amount.

Five organic acids have thus far been studied, and the results are given below. The symbols in the following tables have exactly the same significance as in the preceding. Organic acids being electrolytes, their conductivities were measured. These are recorded in the tables headed "conductivity measurements." v is the volume of the solutions, μ_v their molecular conductivities, and α their dissociation.

Acetic Acid.

Acetic acid being soluble in water in all proportions, we worked to ten-normal concentration. Although the observed freezing-point lowering increased with the concentration, the corrected lowering decreased regularly from the most dilute to the most concentrated solution studied.

The corrected lowering found experimentally was less than the theoretical lowering at all concentrations except the most dilute. This shows that acetic acid in water is polymerized, and that the amount of the polymerization is greater the more concentrated the solution. This is exactly in accord with what was pointed out a year ago by Jones and Murray[1] in their investigation on the effect of one associated liquid on the association of another associated liquid. They showed that water—an associated liquid—diminishes the association of acetic acid—also a strongly associated liquid—and that the magnitude of this effect is a function of the amount of water relative to the amount of acetic acid present. The more concentrated the solution of acetic acid the greater will be the complexity of its molecules. A few of the freezing-point data for acetic acid are plotted in Fig. V. The conductivities of acetic acid are perfectly normal and are plotted in Fig. VI.

Acetic acid shows no evidence of the formation of hydrates except, possibly, in the most dilute solution studied.

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[1] This JOURNAL, 30, 193 (1903).

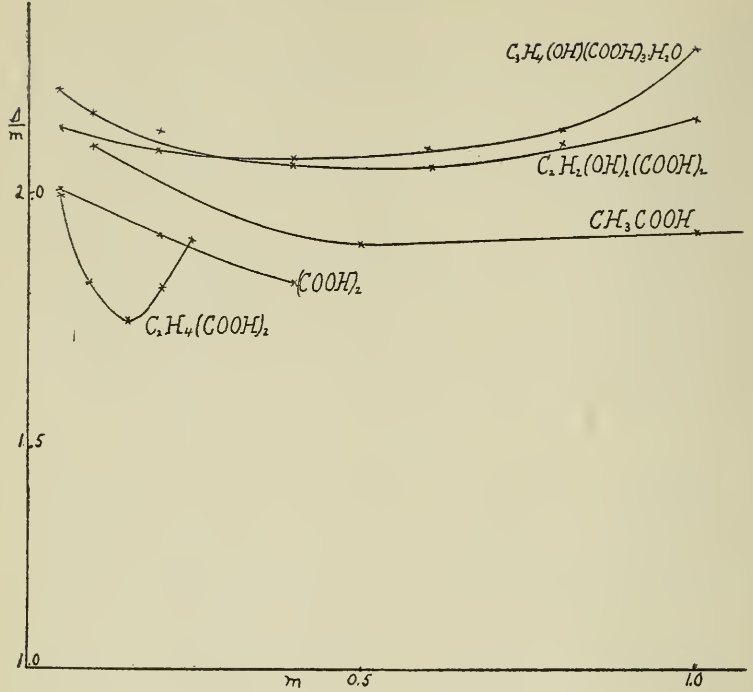
$C_3H_4(OH)(COOH)_3.H_2O$
$\frac{\Delta}{m}$
$C_2H_2(OH)_2(COOH)_2$
2.0
CH_3COOH
$(COOH)_2$
$C_2H_4(COOH)_2$
1.5
1.0
m
0.5
1.0

Fig. V.

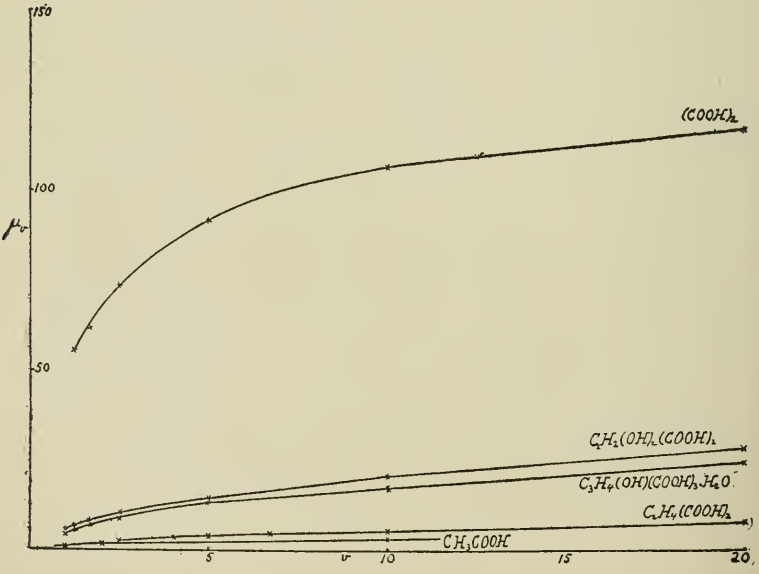
150
$(COOH)_2$
100
μ_v
50
$C_2H_2(OH)_2(COOH)_2$
$C_3H_4(OH)(COOH)_3.H_2O$
$C_2H_4(COOH)_2$
CH_3COOH
5
v
10
15
20

Fig. VI.

Table XL.—Freezing-point Measurements.

Acetic acid, $CH_3.COOH$.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0.210	2.10
0.5	0.945	1.89
1.0	1.908	1.91
2.0	4.000	2.00
3.0	6.190	2.06
4.0	8.260	2.06
5.0	10.500	2.10
6.0	13.000	2.17
7.0	15.200	2.17
8.0	18.000	2.25
10.0	24.000	2.40

Table XLI.—Conductivity Measurements.

Acetic acid, $\mu_v = 2.73$.

v.	μ_v.	α.
0.1	0.04	
0.125	0.07	
0.14	0.10	
0.16	0.14	
0.20	0.19	
0.25	0.25	
0.33	0.35	0.1
0.5	0.52	0.2
1.0	0.85	0.3
2.0	1.33	0.5
10.0	3.07	1.1

Table XLII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	24.9635	0.1500	24.8135	0.75
0.5	25.0450	0.7500	24.2950	2.82
1.0	25.1337	1.5000	23.6337	5.47
2.0	25.3257	3.0000	22.3257	10.70
3.0	25.5228	4.5000	21.0228	15.91
4.0	25.7159	6.0000	19.7159	21.14
5.0	25.8570	7.5000	18.3570	26.57
6.0	26.0329	9.0000	17.0329	31.87
7.0	26.1834	10.5000	15.6834	37.27
8.0	26.2843	12.0000	14.2843	42.86
10.0	26.5551	15.0000	11.5551	53.78

Table XLIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.1	0.010	1.89	2.10	2.08
0.5	0.005	1.87	1.89	1.84
1.0	0.003	1.86	1.91	1.80
2.0	....	1.86	2.00	1.78
3.0	....	1.86	2.06	1.73
4.0	....	1.86	2.06	1.63
5.0	....	1.86	2.10	1.53
6.0	....	1.86	2.17	1.48
7.0	....	1.86	2.17	1.38
8.0	....	1.86	2.25	1.18
10.0	....	1.86	2.40	1.10

Oxalic Acid.

The freezing-point lowerings produced by oxalic acid decrease with increase in concentration, falling below the theoretical value if oxalic acid was not dissociated—Table XLIV. Oxalic acid is, however, very appreciably dissociated, as is shown in Table XLV.

When the corrected molecular lowering L′, Table XLVII., is compared with the molecular lowering L, calculated on the basis of the dissociation of the acid as given in Table XLV., it will be seen that the value found experimentally is much less than the calculated value, at all dilutions studied. This shows that oxalic acid, like acetic acid, undergoes polymerization in solution, and there is no evidence of the existence of hydrates in such solutions. The freezing-point and conductivity data for oxalic acid are given in Figs. V. and VI.

Table XLIV.—Freezing-point Measurements.

Oxalic acid, $(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.101	2.01
0.1	0.207	2.07
0.2	0.382	1.91
0.4	0.725	1.81

Table XLV.—Conductivity Measurements.

Oxalic acid, $\mu_{\infty}^{\circ} = 295$.

v.	μ_v.	α.
1.25	55.4	18.0
1.67	61.66	22.0
2.5	73.75	25.0
5.0	91.44	31.0
10.0	106.5	36.0
20.0	117.8	39.0

Table XLVI.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9785	0.1125	24.8660	0.54
0.1	25.0174	0.2250	24.7924	0.83
0.2	25.1012	0.4500	24.6512	1.40
0.4	25.2235	0.9000	24.3235	2.71

Table XLVII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.05	0.39	3.31	2.01	2.00
0.1	0.36	3.18	2.07	2.05
0.2	0.31	3.01	1.91	1.88
0.4	0.25	2.79	1.81	1.75

Succinic Acid.

The freezing-point lowerings of succinic acid pass through a minimum (Table XLVIII.). The corrected lowerings of succinic acid also pass through a minimum (L′, Table LI.). If the corrected lowerings found experimentally be compared with the lowerings calculated from dissociation, the former will be seen to be always less than the latter. This would show that succinic acid, like oxalic acid, is somewhat polymerized in solution, but the polymerization is less than in the case of oxalic acid.

The freezing-point and conductivity data for succinic acid are plotted in curves, Figs. V. and VI.

Table XLVIII.—Freezing-point Measurements.

Succinic acid, $C_2H_4(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.100	2.00
0.1	0.180	1.80
0.15	0.260	1.73
0.2	0.360	1.80
0.25	0.475	1.90

Table XLIX.—Conductivity Measurements.

Succinic acid, $\mu\infty^\circ = 209$.

v.	μ_v.	α.
2.5	2.54	1.2
4.0	3.46	1.6
5.0	3.94	1.9
6.7	4.54	2.1
10.0	5.33	2.5
20.0	7.30	3.5

Table L.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9731	0.1475	24.8256	0.70
0.10	25.0379	0.2950	24.7429	1.03
0.15	25.0625	0.4425	24.6200	1.44
0.20	25.0839	0.5900	24.4939	2.02
0.25	25.1448	0.7375	24.4073	2.37
0.40	25.2518	1.1800	24.0718	3.71

Table LI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.
0.05	0.035	1.99	2.00	1.99
0.10	0.025	1.95	1.80	1.78
0.15	0.021	1.94	1.73	1.71
0.20	0.019	1.93	1.80	1.74
0.25	0.016	1.92	1.90	1.83

Tartaric Acid.

There is a well-defined minimum in the molecular lowerings, $\frac{\Delta}{m}$, of tartaric acid. This is seen in Table LII., and in Fig. V. The minimum also appears in column L′, Table

LV., which is the molecular lowerings corrected for specific gravities.

The corrected molecular lowerings for tartaric acid are very nearly identical with the molecular lowerings calculated from the dissociation, L, Table LV. This is true for all of the dilutions studied. Tartaric acid is, then, an example of a compound which undergoes neither polymerization nor hydration in solution.

The conductivities of tartaric acid are perfectly normal, as shown by the curve in Fig. VI.

Table LII.—Freezing-point Measurements.

Tartaric acid, $C_2H_2(OH)_2(COOH)_2$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.111	2.22
0.1	0.217	2.17
0.2	0.425	2.13
0.4	0.826	2.06
0.6	1.230	2.05
0.8	1.680	2.10
1.0	2.150	2.15

Table LIII.—Conductivity Measurements.

Tartaric acid, $\mu\infty^\circ = 300$.

v.	μ_v.	α.
1.0	5.76	1.9
1.25	6.69	2.2
1.67	8.02	2.7
2.5	10.13	3.4
5.0	14.34	4.8
10.0	20.54	6.5
20.0	28.05	9.5

Table LIV.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0124	0.1875	24.8249	0.70
0.1	25.0973	0.3750	24.7223	1.11
0.2	25.2584	0.7500	24.5084	1.97
0.4	25.5930	1.5000	24.0930	3.63
0.6	25.9172	2.2500	23.6672	5.33
0.8	26.3938	3.0000	23.3938	6.42
1.0	26.5651	3.7500	22.8151	8.74

Table LV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.
0.05	0.094	2.22	2.22	2.20
0.1	0.065	2.10	2.17	2.15
0.2	0.048	2.04	2.13	2.09
0.4	0.034	1.99	2.06	1.99
0.6	0.027	1.96	2.05	1.94
0.8	0.022	1.94	2.10	1.97
1.0	0.019	1.93	2.15	1.96

Citric Acid.

Column $\frac{\Delta}{m}$, Table LVI., shows a well-defined minimum in the molecular freezing-point lowerings of citric acid. This is seen in the citric acid curve, Fig. V., and in the corrected molecular lowerings for citric acid, L', Table LIX. Citric acid is another example of a compound that shows neither polymerization nor hydration in solution. The corrected experimental values in column L' agree closely with the values calculated from the dissociation of the acid, as given in column L, Table LIX.

The conductivity curve of citric acid is of the same nature and magnitude as that of the other organic acids which we studied with the exception of oxalic acid, which has a much larger conductivity.

Table LVI.—Freezing-point Measurements.

Citric acid, $C_3H_4(OH)(COOH)_3.H_2O$.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.107	2.14
0.1	0.207	2.07
0.2	0.418	2.09
0.4	0.830	2.07
0.6	1.253	2.09
0.8	1.707	2.13
1.0	2.230	2.30

Table LVII.—Conductivity Measurements.

Citric acid, $\mu_{\infty}{}^{\circ} = 630$.

v.	μ_v.	α.
1.0	4.23	0.7
1.25	5.33	0.8
1.67	6.99	1.1
2.5	7.49	1.3
5.0	13.04	2.0
10.0	17.6	2.8
20.0	24.2	3.8

Table LVIII.—Specific Gravities.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.8406	0.2625	24.5781	1.69
0.1	25.1212	0.5250	24.5962	1.61
0.2	25.2869	1.0500	24.2369	3.05
0.4	25.8255	2.1000	23.7255	5.10
0.6	26.0707	3.1500	22.9207	8.32
0.8	26.4768	4.2000	22.2768	9.89
1.0	26.8365	5.2500	21.5865	13.65

Table LIX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.
0.05	0.038	2.07	2.14	2.10
0.1	0.020	2.02	2.07	2.04
0.2	0.020	1.97	2.09	2.03
0.4	0.013	1.93	2.07	1.97
0.6	0.011	1.92	2.09	1.92
0.8	0.008	1.90	2.13	1.92
1.0	0.007	1.89	2.30	1.99

General Conclusions.

1. Of the thirteen non-electrolytes studied in this investigation only glycerol showed any marked hydration or power to combine with the solvent. Glycerol combines with water to about the same extent as the ternary or even some of the quaternary electrolytes.

2. Cane-sugar and fructose also show considerable power to combine with water, but this is not even of the same order of magnitude as that shown by glycerine.

3. Methyl and ethyl alcohol also show some slight power to combine with water in solution.

4. A number of the non-electrolytes studied show a marked tendency to undergo polymerization in the presence of water.

5. The fact that certain non-electrolytes combine with water, forming hydrates, shows that molecules as well as ions can form hydrates, and leaves it an open question as to whether it is the molecules or the ions that combine with water in the case of the electrolytes.

6. None of the organic acids studied in this investigation show any appreciable tendency to combine with water in solution.

7. Some of the organic acids show a marked tendency to undergo polymerization in aqueous solution.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1904.

THE EXISTENCE OF ALCOHOLATES IN SOLUTIONS OF CERTAIN ELECTROLYTES IN ALCOHOL.

BY HARRY C. JONES AND FREDERICK H. GETMAN (CARNEGIE RESEARCH ASSISTANT).

Having found that such a large number of electrolytes[1] and and some non-electrolytes[2] combine with water in aqueous solution, we naturally turned our attention to solutions in solvents other than water. A careful study of some work that we had already done[3] in ethyl alcohol as the solvent, using the boiling-point method, would indicate that certain electrolytes combine with alcohol when in solution in that solvent. An examination of the curves[4] will show that the molecular rise produced by the five electrolytes there studied —sodium bromide, cadmium iodide, potassium iodide, ammonium iodide, and sodium iodide—is greater at some dilution than the theoretical molecular rise in ethyl alcohol. Like the large values found for freezing-point lowering, this indicates that a part of the solvent is combined with the dissolved substance.

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[1] Ztschr. phys. Chem., **46**, 244; Phys. Rev., **18**, 146; This JOURNAL, **31**, 303.

[2] This JOURNAL, **32**, 308.

[3] *Ibid.*, **31**, 338.

[4] *Ibid.*, **31**, 342.

To test this matter still further, other electrolytes have been employed and the molecular rise produced by them carefully measured, using the Jones boiling-point apparatus.[1] The results of these measurements are given below: m is the concentration in terms of gram-molecules of salt in 1,000 grams of solvent, ρ the observed rise in boiling-point, and $\frac{\rho}{m}$ the molecular rise in the boiling-point.

Table I.—LiCl in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.07	0.09	1.28
0.22	0.30	1.37
0.28	0.40	1.43
0.39	0.565	1.45
0.64	0.98	1.53
0.77	1.23	1.58
0.815	1.30	1.59
1.92	1.53	1.66
1.09	1.885	1.73
1.28	2.410	1.89
1.51	3.03	2.00
1.63	3.435	2.10
1.77	3.79	2.14
2.07	5.03	2.43

Table II.—LiCl in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.07	0.09	1.28
0.19	0.255	1.34
0.31	0.44	1.42
0.44	0.65	1.48
0.59	0.91	1.54
0.73	1.145	1.57
0.94	1.59	1.69
1.15	2.10	1.82
1.46	2.95	2.02
1.62	3.42	2.11

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[1] This JOURNAL, **19**, 581.

Table III.—$LiNO_3$ in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.08	0.11	1.38
0.13	0.17	1.30
0.19	0.25	1.31
0.35	0.47	1.34
0.39	0.54	1.38
0.51	0.71	1.39
0.84	1.21	1.44
1.21	1.87	1.54
1.46	2.34	1.60

Table IV.—$LiNO_3$ in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.06	0.085	1.42
0.09	0.120	1.33
0.18	0.234	1.30
0.27	0.355	1.31
0.38	0.515	1.36
0.48	0.655	1.36
0.58	0.810	1.40
0.71	1.010	1.42
0.95	1.415	1.48
1.27	2.010	1.58
1.46	2.385	1.63
1.67	2.770	1.65

Table V.—$Ca(NO_3)_2$ in Ethyl Alcohol. First Series.

m.	ρ.	$\frac{\rho}{m}$.
0.03	0.04	1.33
0.08	0.10	1.25
0.14	0.17	1.21
0.19	0.22	1.16
0.26	0.295	1.13
0.37	0.42	1.13
0.47	0.515	1.09
0.57	0.62	1.08
0.74	0.81	1.09
0.83	0.91	1.09

Table VI.—$Ca(NO_3)_2$ in Ethyl Alcohol. Second Series.

m.	ρ.	$\frac{\rho}{m}$.
0.06	0.08	1.33
0.14	0.17	1.21
0.21	0.21	1.16
0.30	0.34	1.13
0.37	0.40	1.09
0.45	0.50	1.11
0.66	0.71	1.08

The molecular rise in the boiling-point of ethyl alcohol produced by lithium chloride and nitrate is greater at practically all the concentrations studied than would be calculated from its dissociation. Calcium nitrate fulfils this same condition in dilute solutions, but not in concentrated.

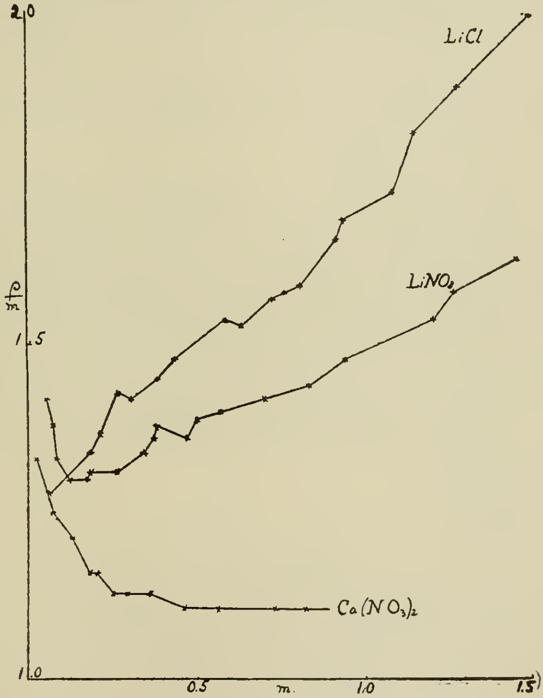

Fig. I.

The results recorded in Tables I. to VI. are plotted as curves, Fig. I. The abscissa represents concentration and the ordinate molecular rise in boiling-point. The curves for the two salts of lithium rise rapidly with increasing concentration, being at practically all concentrations above the calculated curve.

The curve for calcium nitrate in the more dilute solutions rises above the theoretical curve, but rapidly drops to a value agreeing closely with it.

We interpret these results in ethyl alcohol, obtained by the boiling-point method, in the same way that we interpreted the abnormal freezing-point lowerings in water.

The dissolved substance probably combines with a portion of the alcohol, removing it from the field of action as far as rise in boiling-point is concerned. There being, therefore, less alcohol present acting as solvent, the rise in the boiling-point is greater than we would expect from the amount of dissolved substance present.

As far as the formation of alcoholates in solution is concerned, this is, of course, purely qualitative. We hope, however, in the near future, to be able to obtain the data necessary to calculate quantitatively the approximate composition of the alcoholates in such solutions, just as we have already calculated the composition of the hydrates in aqueous solutions of a large number of electrolytes and a few non-electrolytes.

A further study of aqueous solutions, together with solutions in the alcohols and other solvents, will be made as rapidly as possible.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1904.

Contributions from the Sheffield Laboratory of Yale University.

CXIX.—RESEARCHES ON PYRIMIDINES: 2-OXY-4,6-DIAMINOPYRIMIDINE.[1]

[SEVENTH PAPER.]

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

In this paper we describe a number of pyrimidines derived from 2-thiobarbituric acid. Our chief object in investigating these compounds was to prepare 2-oxy-4,6-diaminopyrimidine.

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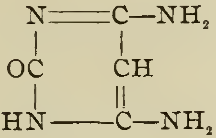
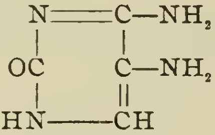
[1] Part of a thesis presented by Mr. G. S. Jamieson for the degree of Doctor of Philosophy, Yale University, 1904.

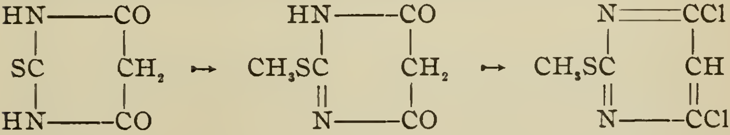
Kutscher[1] believes he obtained an oxydiaminopyrimidine from yeast nucleic acid, the acid having been decomposed by sulphuric acid at a high temperature and under pressure. He considers the substance as differing from cytosine inasmuch as a hydrogen atom is replaced by an amino group.

It may be added that since the pyrimidine derivatives hitherto obtained from nucleic acids have an oxygen atom in the 2-position, for example, uracil, thymine, and cytosine, it is probable that a diamino derivative would be similarly constituted. This being the case, there are only two oxydiaminopyrimidines that fulfil these conditions, namely, 2-oxy-4,6-diaminopyrimidine (I.) and 2-oxy-5,6-diaminopyrimidine (II.) :


I.


II.

Our first attempts to prepare the oxydiaminopyrimidine represented by Formula I. were as follows : 2-Thiobarbituric acid (III.) was prepared by the method of Michael.[2] It was found that this substance could be converted into 2-methylmercapto-4,6-dioxypyrimidine (IV.) by means of sodium ethylate and methyl iodide in alcoholic solution :


III. IV. V.

When the mercapto derivative (IV.) was heated on the steam-bath with 2 molecular proportions of phosphorus pentachloride, it was converted into 2-methylmercapto-4,6-dichlorpyrimidine (V.). The reaction was not smooth and a considerable amount of decomposition-products was always obtained. It was later observed that the dichloride could be obtained more smoothly by using phosphorus oxychloride instead of the pentachloride.

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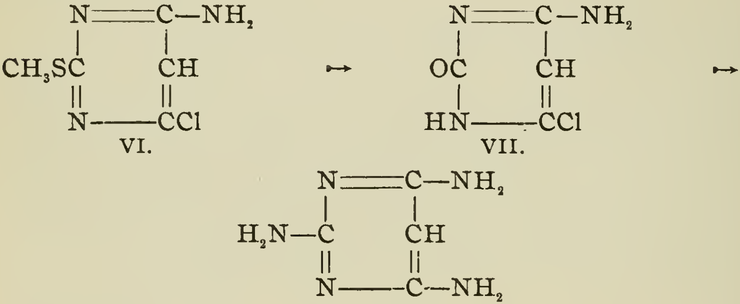
[1] Ztschr. physiol. Chem., 38, 176 (1903).

[2] J. prakt. Chem., 35, 456 (1887) ; 49, 38 (1894).

When the dichloride was heated with alcoholic ammonia it was found that only one chlorine atom was easily removed and 2-mercapto-5-chlorcytosine (VI.) was formed. This took place at temperatures ranging from 125° to about 190°. Even below the latter temperature mercaptan was evolved, and above 190° 2,4,6-triaminopyrimidine (VIII.), which has been described by Gabriel,[1] was obtained. There seemed to be little tendency for the two chlorine atoms to react without also displacing the mercapto group.

The 2-mercapto-4-chlorcytosine was then converted into 4-chlorcytosine (VII.) by boiling with hydrochloric acid. When this was heated with alcoholic ammonia a reaction took place, but the chief product was not the desired 2-oxy-4,6-aminopyrimidine:



VI. VII. VIII.

It was finally found that 2-oxy-4,6-diaminopyrimidine could easily be prepared from 2-thio-4,6-diaminopyrimidine (IX.) which Traube[2] has recently obtained by condensing malonic nitrile with thiourea. This substance united smoothly with methyl iodide and the resulting mercapto derivative (X.) formed on treating the addition-product with ammonia, on carefully boiling with hydrochloric acid, gave the 2-oxy-4,6-diaminopyrimidine (I.):

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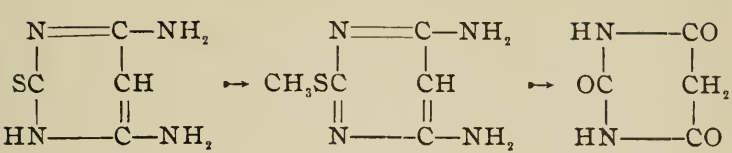
[1] Ber. d. chem. Ges., 34, 3364.

[2] Ann. Chem. (Liebig), 331, 80 (1904).

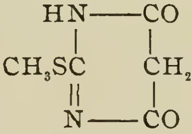


IX. X. XI.

It was then found that if the warming with hydrochloric acid was continued for more than a short time on the steam-bath the 2-oxy-4,6-diaminopyrimidine was completely converted into barbituric acid (XI.). It is therefore obvious, from the readiness with which this compound is decomposed by hydrochloric acid, that it is not identical with Kutscher's new base. If the latter is an oxydiaminopyrimidine it probably is 2-oxy-5,6-diaminopyrimidine.

EXPERIMENTAL PART.

2-Thiobarbituric acid was prepared according to Michael's[1] directions, by the condensation of sodium ethyl malonate with thiourea in absolute alcoholic solution. Twenty-five grams of ethyl malonate gave 20 grams of crude sodium thiobarbiturate. From this a yield of 12 grams of acid was obtained. It was found that if instead of the calculated quantity of sodium ethylate two molecular proportions were used a larger yield of the acid resulted. For example, in two experiments, using 25 grams of ethyl malonate, 27 grams of sodium thiobarbiturate were obtained; in three other cases, using the same proportions, 28 grams of salt separated, the yield of thiobarbituric acid in each case being 16.5 grams.

2-Methylmercaptobarbituric Acid,  .—The best yield of this substance was obtained when 12 grams of thiobarbituric acid were added to a cold, absolute alcoholic solution of 1.9 grams of sodium, then 15 grams of methyl iodide were added and the solution was not allowed to warm. The reaction was complete in two days. The alcohol and excess of methyl iodide were then evaporated and the residue was treated with water and acidified with acetic acid. The precipitate was filtered, washed with water, absolute alcohol, and ether. A yield of 8.6 grams of sodium-free material was obtained. In another experiment, 40 grams of acid gave 2.5 grams of the mercapto derivative, the usual yield being between 53 and 66 per cent of the calculated. Attempts to methylate thiobarbituric acid by other methods, such as by direct addition of methyl iodide, or by the action in alcoholic ammonia, or in aqueous solution and in the presence of alkali, either failed entirely or did not give as satisfactory results as the above method.

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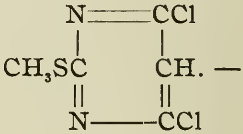
[1] J. prakt. Chem., **35**, 456 (1887); **49**, 38 (1894).

The 2-methylmercaptobarbituric acid crystallized from water in needles. It is sparingly soluble in hot water and less soluble in alcohol. It did not melt at 300°, but gradually turned a light-brown. A nitrogen determination gave:

	Calculated for $C_5H_6O_2N_2S$.	Found.
N	17.72	17.87

2-Methylmercapto-4,6-dichlorpyrimidine,

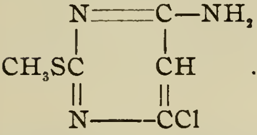


$CH_3SC_4HN_2Cl_2$. —

Four grams of the above 2-methylmercaptobarbituric acid were heated with 9 grams of phosphorus pentachloride on the steam-bath. When the evolution of hydrogen chloride ceased the dark-red solution was cooled and treated with crushed ice. The dichloride was then shaken out with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue distilled at 28 mm. pressure, whereupon 2.5 grams of colorless oil were obtained, boiling at 154°, this being a yield of 50.2 per cent of the calculated. In two other experiments with phosphorus pentachloride, using in each case 8 grams of the methylmercaptobarbituric acid, 3 grams and 3.7 grams of dichloride were obtained. Both specimens boiled at 135° to 136° at 14 mm. pressure. The oil thus obtained solidified in the form of table-like prisms, which melted at 41° to 42°. When phosphorus oxychloride was used instead of the pentachloride, the remaining treatment being the same, the dichloride was directly obtained in the crystalline condition, it being unnecessary to distil under reduced pressure. The material from the ethereal solution was purified by recrystallizing from a little alcohol. It then formed stout, pointed prisms and the melting-point was not altered. It is very soluble in ether, alcohol, and petroleum ether. In two experiments, using 5 grams of the methylmercaptobarbituric acid, 3.3 grams and 3.4 grams of the dichloride were obtained. The yield by the action of either the pentachloride or the oxychloride of phosphorus, especially in large quantities, was found to be very irregular. A nitrogen determination gave:

	Calculated for $C_5H_4N_2SCl_2$.	Found.
N	14.36	14.76

2-Methylmercapto-4-chlor-6-aminopyrimidine,



.—Two and a half grams of the 2-methylmercapto-4,6-dichlorpyrimidine were heated in a sealed tube with about 75 cc. of alcoholic ammonia for four hours at 125° to 126°. On cooling, the ammonium chloride which had separated was filtered and the filtrate evaporated. The residue was purified by recrystallizing from water, in which it was difficultly soluble. It crystallized in colorless, needle-like prisms, which melted at 127° to 128° to a colorless liquid. A yield of 1.5 grams of purified material was obtained. Four other experiments gave the following yields:

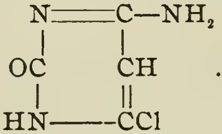
Chloride. Grams.	Monoamine. Grams.
3.7	2.6
3.0	2.2
3.2	2.7
3.3	2.6

A nitrogen determination gave:

	Calculated for $C_5H_6N_3SCl$.	Found.
N	23.93	24.04

Action of Alcoholic Ammonia.—This chloraminopyrimidine (1.1 grams) was heated with about 75 cc. of alcoholic ammonia (alcohol saturated with dry ammonia at 0°) at 145° for three hours and then for two hours at 150°, whereupon the material was recovered completely unaltered. The 1.1 grams of substance were reheated with the same volume of fresh alcoholic ammonia at 170° for two hours, and then at 190° for a half hour; 0.7 gram of unaltered material was obtained.

Two and four-tenths grams of the chloraminopyrimidine were heated with alcoholic ammonia for two hours at 185° to 190°, and four hours at 215° to 220°. On opening the tube the alcohol was found to be saturated with mercaptan. A considerable amount of a light-yellow precipitate had separated from the alcohol. This was filtered, washed with alcohol and then with water. It melted at about 234° to 240° and it gave an alkaline reaction to turmeric paper. It contained neither sulphur nor chlorine and was found to be 2,4,6-triaminopyrimidine, which has been described by Gabriel.[1]

4-Chlorcytosine,  .—This was obtained by boiling 0.5 gram of the above mercapto derivative with concentrated hydrochloric acid. Mercaptan was readily evolved and upon evaporating the solution, 4-chlorcytosine hydrochloride was obtained. This crystallized from hot water in balls of very small, slender, hard prisms or needles. From dilute aqueous solutions of this salt, ammonia precipitates a crop of flat, colorless prisms; from more concentrated solutions the base separates as a jelly resembling thick starch paste, which is difficult to filter. When dried on paper it adheres strongly to the fiber. It is fairly soluble in water and it does not melt at 300°, although it sinters and gradually turns red. A nitrogen determination gave:

	Calculated for $C_4H_4ON_3Cl$.	Found.
N	28.86	28.73

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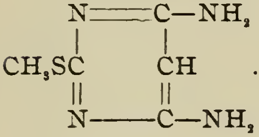
[1] Ber. d. chem. Ges., **34**, 3364.

The chlorine in this compound is very firmly bound. It was not removed by tin and hydrochloric acid, or by red phosphorus and hydriodic acid.

When 1.5 grams of this material were heated with alcoholic ammonia at 183° for two hours 0.95 gram of substance insoluble in alcoholic ammonia was formed. It was difficultly soluble in water; if the solution was cooled rapidly, very small crystals were obtained; if slowly cooled, little balls were formed. This substance did not melt at 307°. It was free from chlorine and a nitrogen determination gave only 24.9 per cent nitrogen. It was not identified, since two attempts to prepare the compound failed on account of the explosion of the sealed tubes and no time was available to repeat the work.

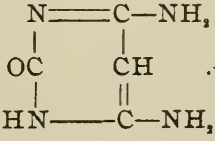
2-Methylmercapto-4,6-diaminopyrimidine,



.—Malonic nitrile and thiourea were condensed according to Traube's[1] directions in an alcoholic solution with sodium ethylate. Two grams of the 2-thio-4,6-diaminopyrimidine were moistened with alcohol and 2.2 grams of methyl iodide were added. The mixture stood two hours without change. Suddenly, heat was evolved and the solution solidified. The alcohol was evaporated and the residue was dissolved in water. Ammonia then precipitated 2.2 grams of colorless crystalline material. This was quite soluble in hot water, from which, on cooling, it separated in the form of slender prisms. It melted at 185° to 186° with a little effervescence, and a nitrogen determination gave:

	Calculated for $C_5H_8N_4S$.	Found.
N	35.89	35.94

2-Oxy-4,6-diaminopyrimidine,



.—One gram

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[1] Ann. Chem. (Liebig), 331, 80 (1904).

of the 2-methylmercapto-4,6-diaminopyrimidine was evaporated twice with about 20 cc. of concentrated hydrochloric acid on the steam-bath. Methylmercaptan was evolved and the residue crystallized from water. The monohydrochloride which separated formed long, slender prisms which did not melt at 307°. This salt was dissolved in water and an excess of ammonium hydroxide was added, whereupon a fine crystalline meal was precipitated. It was difficultly soluble in hot water, and it separated as slender, rectangular, anhydrous prisms. When the material was heated it became gradually yellow at about 297° and remained a dry, yellow powder at 347°. A nitrogen determination gave :

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	44.82

The *picrate* separated from hot water when slowly cooled in the form of thin tables. If rapidly cooled it formed bunches of slender prisms. It had a bright yellow color, and a nitrogen determination showed that it was a monopicrate :

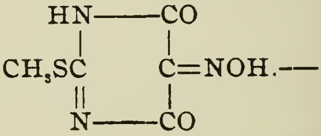
	Calculated for $C_{10}H_9O_8N_7$.	Found.
N	27.60	27.46

It sinters at about 185° and melts with effervescence at 210° to 214°.

It was found that if the 2-methylmercapto-4,6-diaminopyrimidine was warmed with hydrochloric acid for a longer time than was sufficient to expel the mercaptan, barbituric acid was obtained. This was identified by its crystallizing with water of crystallization and by the following nitrogen determination in the dried material :

	Calculated for $C_4H_4O_2N_2$.	Found.
N	21.89	22.36

2-Methylmercaptovioluric Acid,

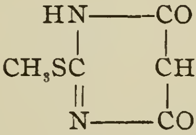


Eight grams of 2-methylmercapto-4,6-dioxypyrimidine were dissolved in 150 cc. of water containing 2 grams of sodium hydroxide. Four grams of sodium nitrite were added and the solution was acidified with acetic acid. The solution turned dark-blue when acidified, but gradually became red. A brick-red precipitate formed after the solution stood ten hours and 4.55 grams of the isonitrosopyrimidine were obtained, or 48 per cent of the calculated. It became dark-colored when heated and gradually decomposed at 180° to 200°. The ammonium and sodium salts have a purple color. Some of the sodium salt was dissolved in warm water and acidified with hydrochloric acid. The solution became red, and, on standing, it deposited red, flat, pointed prisms, which contained 2 molecules of water of crystallization. The water was determined by heating the material at 120°.

	Calculated for $C_5H_6O_3N_3S.2H_2O$.	Found.
H_2O	11.66	11.84

A nitrogen determination in the case of the anhydrous material gave:

	Calculated for $C_5H_5O_3N_3S$.	Found.
N	22.46	22.22

2-Methylmercaptouramil,  —This was obtained from the above isonitrosopyrimidine by reduction with ammonium sulphide according to Traube's method.[1] This material is difficultly soluble in water or hydrochloric acid, dilute or concentrated. It is soluble in sodium hydroxide and it is precipitated by acetic acid, in which it is difficultly soluble. A nitrogen determination gave:

	Calculated for $C_5H_7O_2N_3S$.	Found.
N	24.28	24.37

Attempts to chlorinate this material by means of phosphorus oxychloride did not lead to a smooth result. The material turns brown on heating at 285° but does not melt at 301°.

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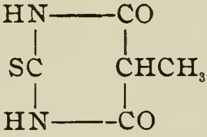
[1] Ann. Chem. (Liebig), **331**, 82 (1904).

The following pyrimidine derivatives were prepared by Dr. Henry F. Merriam in the course of some work on isomers of histidine. The work was interrupted by the departure of Mr. Merriam from this laboratory.

2-Thio-5-methylbarbituric Acid,  — Seven and eight-tenths grams of sodium were dissolved in alcohol and the solution added to 60 grams of methylmalonic ethyl ester. A hot alcoholic solution of 26 grams of thiourea was then added and the mixture heated gently on the steam-bath for five hours. The white sodium salt was then filtered, dissolved in a small volume of hot water, and the solution acidified strongly with hydrochloric acid. On cooling, a mass of thin plates separated. After crystallizing from water the substance melted with effervescence at about 244.° The yield was 27 grams. 2-Thio-5-methylbarbituric acid crystallizes with 1 molecule of water of crystallization, which is evolved at 120°.

	Calculated for $C_5H_6O_2N_2S.H_2O$.	Found.
H_2O	18.55	18.25

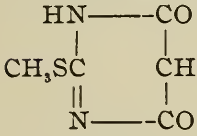
A nitrogen determination in the case of the dried material gave:

	Calculated for $C_5H_6O_2N_2S$.	Found.
N	17.72	18.04

2-Thio-5-ethylbarbituric Acid.—An alcoholic solution of 11 grams of sodium was added to 90 grams of ethylmalonic ethyl ester and a solution of 37 grams of thiourea in hot alcohol was added to the mixture, which was then warmed on the steam-bath for several hours. The white sodium salt was then removed by filtering and the free acid was liberated by means of hydrochloric acid. It separated from water in the form of long, needle-like prisms and it melted at 190° to 191°. It is soluble in alcohol. The yield was 37 grams. It contains water of crystallization, which is given off at 120°. A nitrogen determination in the dry material gave :

	Calculated for $C_6H_8O_2N_2S$.	Found.
N	16.27	16.53

2-Methylmercapto-4,6-dioxy-5-methylpyrimidine,



$$\begin{array}{ccc} & HN\text{——} & CO \\ & | & | \\ CH_3SC & & CHCH_3 \\ & \| & | \\ & N\text{——} & CO \end{array}$$

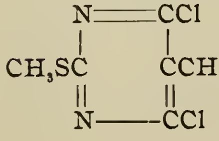
.—This compound was prepared by boiling 2-thio-5-methylbarbituric acid with alcohol and an excess of methyl iodide. After several hours the solid material was filtered and washed with alcohol. The material was almost insoluble in water and alcohol and it was purified by crystallizing from strong acetic acid. It formed short prisms which, on heating, decomposed with effervescence at about 303°. From 28 grams of thiomethylbarbituric acid 18.5 grams of the mercapto compound were obtained.

	Calculated for $C_6H_8O_2N_2S$.	Found.
N	16.27	16.23

2-Methylmercapto-4,6-dioxy-5-ethylpyrimidine. — Thirty-six grams of 5-ethylthiobarbituric acid, treated in the same manner as the above, except that in this case, after the action was complete, most of the alcohol was evaporated and the residue was treated with water, gave 25 grams of the mercapto compound. After crystallizing from acetic acid it melted with effervescence at about 257°. It was easily soluble in alcohol and acetic acid and difficultly soluble in water. A nitrogen determination gave :

	Calculated for $C_7H_{10}O_2N_2S$.	Found.
N	15.05	15.19

2-Methylmercapto-4,6-dichlor-5-methylpyrimidine,



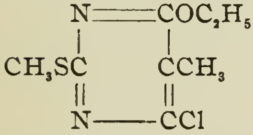
$$\begin{array}{ccc} & N\text{===} & CCl \\ & | & | \\ CH_3SC & & CCH_3 \\ & \| & \| \\ & N\text{——} & CCl \end{array}$$

.—Ten and three-tenths grams of 2-methylmercapto-4,6-dioxy-5-methylpyrimidine were heated on the steam-bath with 12.7 grams of phosphorus pentachloride. The material melted and, finally, the phosphorus oxychloride was removed by distilling in a vacuum. The residue was treated with ice-water and ether and the ethereal solution was dehydrated and distilled at 18 mm. pressure. The dichloride then boiled at 153° to 154°, and, on cooling, it crystallized in the form of colorless, stout prisms melting at 64°. The yield was 10.3 grams and a nitrogen determination gave :

	Calculated for $C_6H_6N_2SCl_2$.	Found.
N	13.39	13.48

As in the case of 2-methylmercapto-4,6-dichlorpyrimidine, only one chlorine atom is especially reactive in this compound.

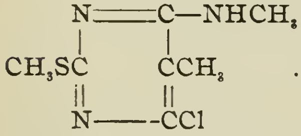
2-Methylmercapto-4-chlor-5-methyl-6-ethoxypyrimidine,



.—Seven grams of the above dichloride were dissolved in alcohol and 0.9 gram of sodium in alcoholic solution was added. The mixture was warmed for an hour on the steam-bath. The material was then precipitated with water and crystallized from alcohol, whereupon beautiful, colorless prisms were obtained melting at 85°. This substance is readily soluble in alcohol and benzene and insoluble in water. The yield was 6 grams. A nitrogen determination gave :

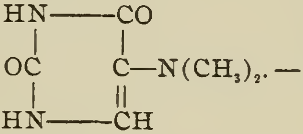
	Calculated for $C_8H_{11}ON_2SCl$.	Found.
N	12.81	13.18

2-Methylmercapto-4-chlor-5-methyl-6-methylaminopyrimidine,



.—Nine grams of the above dichlor compound were heated at 145°, for three hours, with 5 grams of methylamine in 58 cc. of alcohol. The solution was then evaporated, the residue washed with water and crystallized several times from alcohol. It formed stout prisms, which melted at 157°. The reaction was not complete and the yield was 5 grams. A nitrogen determination gave:

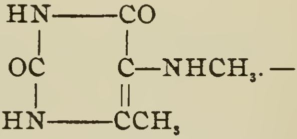
	Calculated for $C_7H_{10}N_3ClS$.	Found.
N	20.64	20.96

5-Dimethylaminouracil, 

$$\begin{array}{lcl} \mathrm{HN} & \text{——} & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & \mathrm{C{-}N(CH_3)_2} \\ | & & \| \\ \mathrm{HN} & \text{——} & \mathrm{CH} \end{array}$$

— This compound, isomeric with histidine, was prepared by heating 5-bromuracil[1] with an excess of dimethylamine at 150° for six hours. The contents of the tube were evaporated, taken up in water, and boiled with animal charcoal. The material was then crystallized from water, in which it is moderately soluble when hot, and very difficultly soluble when cold. It formed small, thin, colorless plates or films, which melted with strong effervescence at about 297°. A nitrogen determination gave:

	Calculated for $C_6H_9O_2N_3$.	Found.
N	27.09	27.23

4-Methyl-5-methylaminouracil, 

$$\begin{array}{lcl} \mathrm{HN} & \text{——} & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & \mathrm{C{-}NHCH_3} \\ | & & \| \\ \mathrm{HN} & \text{——} & \mathrm{CCH_3} \end{array}$$

— Fifteen grams of 4-methyl-5-bromuracil, prepared according to the directions of Behrend,[2] were heated for six hours at 150° with an excess of aqueous methylamine. The contents of the tube were then heated on the steam-bath until the free methylamine was removed. The bromine was removed by means of silver sulphate, the excess of silver by hydrogen sulphide, and the sulphuric acid by barium hydroxide, and the excess of the latter was precipitated by carbon dioxide. Then, on concentrating the solution to a small volume, a beautiful crop of colorless prisms separated. After crystallizing from water containing a little alcohol the compound melted at 214°. When crystallized from water, in which it is very soluble, it contains 1 molecule of water of crystallization. The presence of much alcohol in the water causes the compound to crystallize in an anhydrous condition. Water was determined by heating the material at 120°.

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[1] Wheeler and Merriam: This JOURNAL, **29**, 486 (1903).

[2] Ann. Chem. (Liebig), **231**, 249.

	Calculated for $C_6H_9O_2N_3.H_2O$.	Found.
H_2O	10.40	10.26

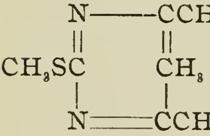
A nitrogen determination in the case of the dried material gave :

	Calculated for $C_6H_9O_2N_3$.	Found.
N	27.09	27.25

The *monohydrochloride* was prepared by dissolving the base in dilute hydrochloric acid and evaporating the solution. It formed beautiful, transparent, stout prisms, which melted at 273° with strong effervescence. The hydrochloride was less soluble in water than the free base, and the following analysis showed that the salt was anhydrous :

	Calculated for $C_6H_9O_2N_3.HCl$.	Found.
N	21.93	22.27

2-Methylmercapto-4,6-dimethylpyrimidine,



.—(By G. S. Jamieson.) Thirty-five grams of the methyl iodide addition-product of thiourea were dissolved in 30 cc. of water containing 9 grams of potassium hydroxide and 16 grams of acetylacetone were then added. The latter dissolved when the solution was shaken vigorously for a few seconds. The clear solution gradually became turbid, and, after standing for two days, a dark-yellow oil separated. This was shaken out with ether and the ethereal solution was dehydrated over potassium hydroxide. The oil was then distilled at 28 to 29 mm. pressure, whereupon it boiled at 135° to 137°, leaving a notable residue. Six grams of colorless, odorless oil were obtained, a yield of 24.4 per cent of the calculated. Another condensation was made with three times the above quantities and 17.7 grams of oil were obtained which boiled at 144° at 33 mm. pressure and at 123° to 125° at 14 mm. pressure. The yield in this case was 23.9 per cent of the calculated. When the oil was cooled it solidified to a white, ice-like mass and melted at about 23° to 24°. The material is moderately soluble in cold water, and when the solution is warmed the substance separates in the form of oil drops, which dissolve again on cooling. It appears to absorb moisture from the air, since only by drying over sulphuric acid could agreeing results be obtained on analysis. Nitrogen determinations then gave:

	Calculated for $C_7H_{10}N_2S$.	Found. I.	II.
N	18.18	18.22	18.32

The residue, obtained as a by-product in this preparation, was not distilled, but when crystallized from alcohol, in which it was very soluble, it separated in the form of colorless, rectangular prisms, which melted at 153° to 154° to a clear liquid. A nitrogen determination agreed with the calculated for a dicyandiamide addition-product of 2-methylmercapto-4,6-dimethylpyrimidine or an isomer. It was not further examined.

2-Oxy-4,6-dimethylpyrimidine.—The above mercapto derivative, melting at 23° to 24°, was boiled with hydrobromic acid for three hours, evaporated, taken up in water, and neutralized with alkali. It was again evaporated and the dried, powdered material was extracted with benzene containing alcohol. The extracted material was crystallized twice from water, in which it was easily soluble. It melted at 198° to 199°. Evans[1] gives the melting-point of this substance, which he prepared by a different method, at 190° to 195°. Our material was shown to be identical with that of Evans by preparing the bromine derivative melting at 145° and by its behavior with diazobenzene chloride.

NEW HAVEN, CONN., June, 1904.

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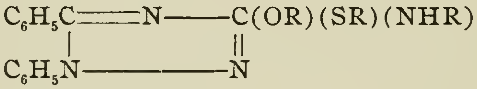
[1] J. prakt. Chem., 48, 489 (1893).

Contributions from the Sheffield Laboratory of Yale University.

CXX.—ON THE ACTION OF PHENYLHYDRAZINE ON BENZOYLPSEUDOUREAS: 1,5-DIPHENYL-3-AMINOPYRRO-α,β′-DIAZOLE DERIVATIVES.

By Treat B. Johnson and George A. Menge.

Several papers[1] have appeared from this laboratory describing the behavior of phenylhydrazine towards acylthiocarbamates, RCO.NHCSOR, RCONHCOSR, acyldithiocarbamates, RCONHCSSR, acylimidothiocarbonates, RCON$=$C(OR)(SR), and acylimidodithiocarbonates, RCON$=$C(SR)$_2$. In every case that has been examined 1,5-dialkyltriazoles (Formula I.) have been the products of the reaction:



I.

One would be led to believe from these results that the relative tendency of the groups—CSalk., CS, CO, COalk.—to react with the hydrogen of the amino group in phenylhydrazine can be expressed by the following arrangement:

$$\text{CSalk.} > \text{CS} > \text{CO} > \text{COalk.}$$

It seemed of interest to decide whether the above rule would hold in other types of compounds containing these groups, or whether it is a general tendency for 1,5-dialkyltriazoles to form in preference to the 1,3-dialkyltriazoles.

The acyloxygenpseudoureas—RCON$=$C(OR)NH$_2$—should yield 1,3-dialkyltriazoles according to the above representation, since water is represented as separating in preference to alcohol.

We find that the acyloxygenpseudoureas react less readily with phenylhydrazine than the other types of derivatives which have been examined. The acylpseudothioureas react at ordinary temperature with phenylhydrazine, while the acyloxygenpseudoureas remain unaltered under the same conditions. They react smoothly, nevertheless, when heated to 130° to 150°, and give 1,5-dialkyltriazoles analogous to the acylpseudothioureas. The same triazole was obtained by heating phenylhydrazine with benzoylpseudoethylphenylurea as was obtained by Wheeler and Beardsley[1] from phenylhydrazine and benzoylthiolethylphenylpseudothiourea :

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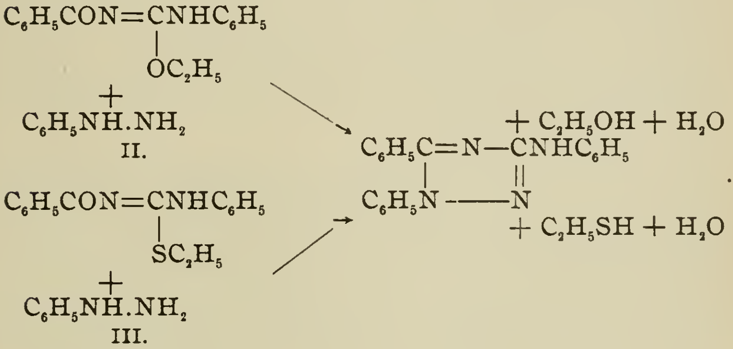
[1] Wheeler and Johnson: This Journal, **24**, 198 (1900); Wheeler and Beardsley: *Ibid.*, **27**, 258 (1902); **29**, 74 (1903).



$$\begin{array}{lll} C_6H_5CON{=}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}NHC_6H_5 & & + C_2H_5OH + H_2O \\ + & \searrow & \\ C_6H_5NH.NH_2 \quad \text{II.} & & C_6H_5C{=}N{-}CNHC_6H_5 \\ & & \quad | \qquad\quad \| \\ C_6H_5CON{=}\underset{\displaystyle SC_2H_5}{\underset{|}{C}}NHC_6H_5 & \nearrow & C_6H_5N{-}{-}{-}N \\ + & & + C_2H_5SH + H_2O \\ C_6H_5NH.NH_2 \quad \text{III.} & & \end{array}$$

This behavior of the oxygenpseudoureas presents the first exception observed to the above rule. Apparently, from this there is a tendency for the 1,5-dialkyltriazoles to form rather than 1,3-dialkyltriazoles, and that the reaction does not necessarily proceed according to the above arrangement.

Wheeler and Beardsley[1] have prepared 1,3-diphenyl-5-mercaptotriazole by warming formylphenylhydrazine with benzoyl rhodanide and then treating the material with cold alkali. This reaction was not smooth and the triazole was always obtained mixed with secondary products.

We find that this triazole can be prepared very easily by combining benzoyl rhodanide with acetonephenylhydrazone. When the resulting semicarbazide was treated with dilute hydrochloric acid, or boiled with water, it was converted quantitatively into the 1,3-diphenyl-5-mercaptotriazole (Formula V.) :

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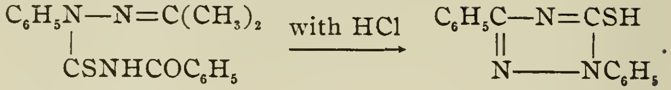
[1] *Loc. cit.*

$C_6H_5NH.N{=}C(CH_3)_2 + C_6H_5CONCS\ =$



$$\underset{\text{IV.}}{\begin{array}{l}C_6H_5N{-}N{=}C(CH_3)_2\\ \quad|\\ \quad CSNHCOC_6H_5\end{array}} \xrightarrow{\text{with HCl}} \underset{\text{V.}}{\begin{array}{l}C_6H_5C{-}N{=}CSH\\ \quad\ \|\qquad\quad |\\ \quad\ N{-\!-\!-}NC_6H_5\end{array}}\ .$$

IV. V.

The behavior of the above semicarbazide (Formula IV.) towards hydrochloric acid and water is similar to an observation made by Arnold.[1] He found that cyanic acid readily combined with acetonephenylhydrazone to give the acetone derivative of unsymmetrical phenylsemicarbazide. When this acetone derivative was boiled with water it was converted into phenylsemicarbazide.

The behavior of the two above semicarbazides is in striking contrast to an earlier observation made by Vahle.[2] He showed that phenyl mustard-oil combined with acetonephenylhydrazone to form the acetone derivative of *a*,*b*-diphenylthiosemicarbazide. This compound was soluble in acids, and after prolonged boiling with strong hydrochloric acid could be precipitated unaltered from its acid solution.

Dixon[3] has investigated the action of phenylhydrazine on benzoyl rhodanide. He described the product formed as benzoylphenylthiosemicarbazide, and states that it does not melt at 220°.

We find that phenylhydrazine reacts with benzoyl rhodanide to form four definite products. Three of these we have been able to separate in a state of purity. Benzoylphenylthiosemicarbazide (Formula VI.) was isolated, which melted at 136° and not at 220°. Associated with the thiosemicarbazide was 1,5-diphenyl-3-mercaptotriazole (Formula VIII.), melting at 187°, and also 1,3-diphenyl-5-mercaptotriazole (Formula IX.), melting at 248°. We did not succeed in isolating the fourth product formed in this reaction (Formula VII.) :

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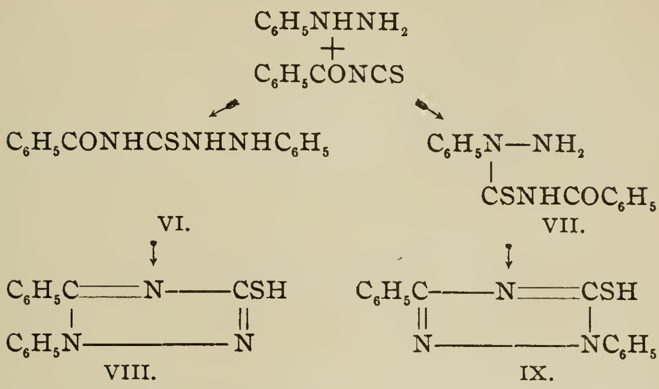
[1] Ber. d. chem. Ges., **30**, 1016.

[2] *Ibid.*, **27**, 1514.

[3] J. Chem. Soc. (London), **55**, 304.



Benzoylphenylthiosemicarbazide (Formula VI.) was previously obtained in this laboratory[1] by treating ethyl benzoyldithiocarbamate with phenylhydrazine at ordinary temperature. It melted at 136° and agreed in none of its properties with Dixon's supposed thiosemicarbazide. When heated above its melting-point it was converted into 1,5-diphenyl-3-mercaptotriazole, melting at 187°.

The formation of the two isomeric triazoles in the above reaction again show the strong tendency of phenylhydrazine to offer two points of attack towards reactive substances. The action of benzoyl rhodanide is perfectly analogous to the behavior of phenylhydrazine towards benzanilideimide chloride which was recently examined by Wheeler and Johnson.[2] This interesting behavior has also been observed by other investigators.[3]

The ease with which the acylimidothiocarbonates, RCON=C(OR)(SR), and acylimidodithiocarbonates, RCON=C(SR)$_2$, react with amines to form pseudoureas, suggested that they would react with the basic, non-substituted pseudothioureas to form triazine derivatives, as follows:

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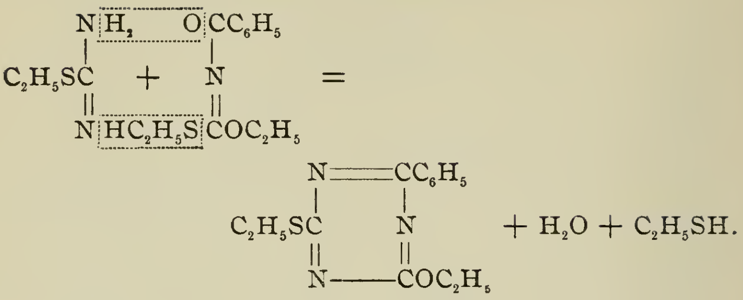
[1] Wheeler and Beardsley: *Loc. cit.*

[2] This JOURNAL, **31**, 578.

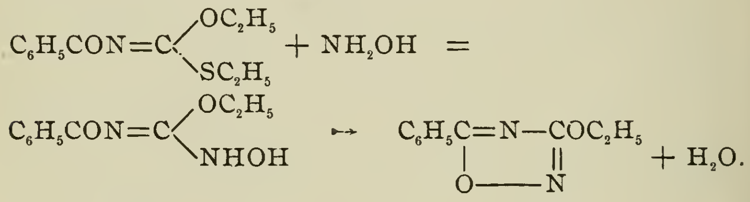
[3] Busch: Ber. d. chem. Ges., **34**, 322; **36**, 3877; Frerich and Beckurts: Arch. Pharm., **237**, 346.



X.

We find that pseudoethylthiourea combines with benzoylimidodiethylthiocarbonate at ordinary temperature. We were able to isolate a beautiful crystalline product melting at 48°. A nitrogen determination agreed with the calculated for ethylmercaptoethoxyphenyl-1,3,5-triazine (Formula X.).

One might expect hydroxylamine to react with an acylimidothiocarbonate to form a substituted acylpseudourea (Formula XI.), which could then condense to a furo-α,β'-diazole (Formula XII.) as follows:



XI. XII.

We find that hydroxylamine reacts with benzoylimidodiethylthiocarbonate in alcoholic solution at ordinary temperature. Much heat was evolved, and mercaptan was given off immediately. We were able to isolate a product which melted at 48°, and a nitrogen determination agreed with the calculated for α'-phenyl-β-ethoxyfuro-α,β'-diazole (Formula XII.).

An isomeric oxyethylphenylfuro-α,β'-diazole has been prepared by Falck.[1] He obtained it by acting on the silver salt of α'-oxy-β-phenylfuro-α,β'-diazole with ethyl iodide at 100°.

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[1] Ber. d. chem. Ges., 18, 2467; 19, 1481.

He states that it melts at 36°, but represents it with the alkyl group attached to nitrogen instead of oxygen. From work that has appeared from this laboratory[1] on the molecular rearrangement of imidoesters one might expect that a nitrogen alkyl derivative would be formed under the conditions that Falck obtained his furo-α,β'-diazole.

We have repeated Falck's experiments and find that the same ethyl derivative is formed when ethyl iodide is allowed to act on the silver salt at ordinary temperature. We feel justified in concluding from this result, and from previous work on the structure of silver salts and their behavior towards alkyl halides,[2] that the ethyl radical in Falck's furo-α,β'-diazole is attached to oxygen and not to nitrogen.

We also found that the acyloxygenpseudoureas react with great ease with hydroxylamine. Benzoylpseudoethylphenylurea and hydroxylamine reacted at once when heated in alcoholic solution to about 50°. A beautiful crystalline compound was formed, and a nitrogen determination agreed with the calculated for a furo-α,β'-diazole derivative. On account of lack of time the structure of these derivatives obtained with hydroxylamine must be decided at a later date.

Sell and Zierold[3] obtained the chloride of phenyl isocyanate by leading chlorine gas into a chloroform solution of phenyl mustard-oil. Nef[4] also obtained the same chloride by using phenyl isocyanate instead of phenyl mustard-oil.

We find that benzoyl rhodanide reacts as readily with chlorine gas as phenyl mustard-oil. The chloride is a light-yellow oil which can be distilled under diminished pressure without decomposition. It is a most intensely reactive body and combines with violence with water, alcohol, and amines. We expect to investigate some of the reactions of this interesting substance.

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[1] Wheeler and Johnson : This JOURNAL, **21**, 186 ; Wheeler : *Ibid.*, **23**, 136.

[2] Nef : Ann. Chem. (Liebig), **266**, 66 ; **276**, 235. Tafel and Enoch : Ber. d. chem. Ges., **23**, 104, 1550. Comstock and Kleeberg ; This JOURNAL, **12**, 493 ; Comstock and Wheeler : *Ibid.*, **13**, 520. Stieglitz and Dains : J. Am. Chem. Soc., **21**, 187 : Wheeler and Johnson : This JOURNAL, **30**, 32. Slimmer and Stieglitz : *Ibid.*, **31**, 666.

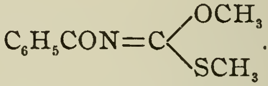
[3] Ber. d. chem. Ges., **7**, 1228.

[4] Ann. Chem. (Liebig), **270**, 282.

EXPERIMENTAL PART.

The acyloxygenpseudoureas described in this paper were prepared by allowing amines to act on acylimidothiocarbonates at ordinary temperature. Certain representatives[1] of this class of derivatives have previously been described as oils. Recently Bruce[2] has prepared a series of these pseudoureas, which he has described as well-crystallized substances. The acyloxygenpseudoureas that we have prepared show little tendency to crystallize, small traces of impurity causing them to remain as oils for weeks. When obtained in a state of purity they form beautiful crystalline compounds, which are comparatively stable and can be recrystallized from the ordinary solvents.

Benzoylimidodimethylthiocarbonate,

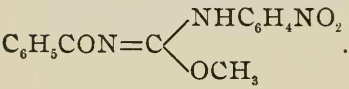


$C_6H_5CON{=}C\left\langle\begin{matrix}OCH_3\\SCH_3\end{matrix}\right.$.—

This substance,[3] previously obtained as an oil, was prepared by dissolving methylbenzoylthioncarbamate and a molecular proportion of sodium ethylate in cold alcohol and then adding a molecular proportion of methyl iodide. We observed that the thiocarbonates were obtained much purer if the reaction was allowed to proceed at very low temperatures. It was separated from the alcohol by precipitating with water. It boiled at 200° at 20 mm. pressure. It solidified on cooling, and crystallized from ligroin in colorless prisms melting at 43°. A nitrogen determination gave:

	Calculated for $C_{10}H_{11}O_2NS$.	Found.
N	6.70	7.00

Benzoylpseudomethyl-m-nitrophenylurea,



$C_6H_5CON{=}C\left\langle\begin{matrix}NHC_6H_4NO_2\\OCH_3\end{matrix}\right.$.—This pseudourea[4] was previously obtained as an intermediate product in the preparation of benzoylnitrophenylurea from metanitroaniline and benzoylimidomethylthiolethylcarbonate. We have now isolated this pseudourea in a state of purity and find that it crystallizes from alcohol in needle-like prisms, and melts at 86° to 88°. A nitrogen determination gave:

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[1] Wheeler and Johnson: This JOURNAL, **24**, 190; McKee: *Ibid.*, **26**, 209.

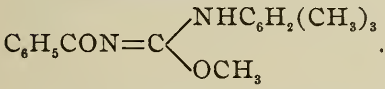
[2] J. Am. Chem. Soc., **26**, 419.

[3] Wheeler and Johnson: This JOURNAL, **24**, 190.

[4] *Loc. cit.*

	Calculated for $C_{15}H_{13}O_4N_3$.	Found.
N	14.05	14.20

Benzoylpseudomethylpseudocumylurea,

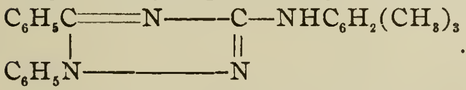


$$C_6H_5CON{=}C\begin{cases}NHC_6H_2(CH_3)_3\\OCH_3\end{cases}$$

.—From pseudocumidine and benzoylimidomethylthiolethylcarbonate. It crystallized from alcohol in beautiful, needle-like prisms and melted at 87° to 89°. It was very soluble in ether and benzene. A nitrogen determination gave:

	Calculated for $C_{18}H_{20}O_2N_2$.	Found.
N	9.46	9.38

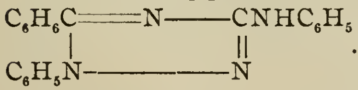
1,5-Diphenyl-3-pseudocumylaminotriazole,



.—This triazole was obtained when the above benzoylpseudomethylpseudocumylurea was warmed for several hours at 130° with a molecular proportion of phenylhydrazine. On allowing the melt to stand for several hours at ordinary temperature it finally solidified. The triazole crystallized from alcohol in rosettes of needle-like prisms and melted at 121° to 123°. A nitrogen determination gave:

	Calculated for $C_{23}H_{22}N_4$.	Found.
N	15.82	16.2

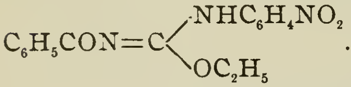
1,5-Diphenyl-3-phenylaminotriazole,



.—This was obtained by heating phenylhydrazine with benzoylpseudoethylphenylurea at 120° to 130°. It crystallized from alcohol in needles and melted at 202°. The triazole was previously obtained by Wheeler and

Beardsley[1] by treating benzoylphenylthiolethylpseudothiourea with phenylhydrazine. When their triazole was mixed with our triazole melting at 202° the melting-point was not lowered.

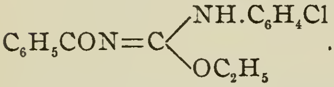
Benzoylpseudoethyl-m-nitrophenylurea,



$C_6H_5CON{=}C\Big\langle\begin{array}{l}NHC_6H_4NO_2\\ OC_2H_5\end{array}$.—From metanitroaniline and benzoylimidodiethylthiocarbonate. After heating for a few hours at about 75° a thick oil was obtained which finally solidified. It crystallized from alcohol in the form of prisms and melted at 86° to 88°. A nitrogen determination gave :

	Calculated for $C_{16}H_{15}O_4N_3$.	Found.
N	13.4	13.31

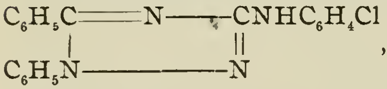
Benzoylpseudoethyl-m-chlorphenylurea,



$C_6H_5CON{=}C\Big\langle\begin{array}{l}NH.C_6H_4Cl\\ OC_2H_5\end{array}$.—From metachloraniline and benzoylimidodiethylthiocarbonate. After standing two weeks the pseudourea separated in the form of large prisms. It crystallized from alcohol in long, slender prisms and melted at 47° to 48°. A nitrogen determination gave :

	Calculated for $C_{16}H_{15}O_2N_2Cl$.	Found.
N	9.23	9.53

1,5-Diphenyl-3-m-chlorphenylaminotriazole,



, was obtained by heating phenylhydrazine with benzoylpseudoethyl-*m*-chlorphenylurea at 120° to 130° for seven hours. The triazole crystallized after standing several hours at ordinary temperature. It crystallized from absolute alcohol in short, stout prisms, and melted at 195° to 196°. A nitrogen determination gave :

	Calculated for $C_{20}H_{15}N_4Cl$.	Found.
N	16.16	16.26

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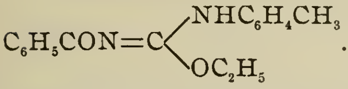
[1] *Loc. cit.*

Benzoylpseudoethylparatolylurea,

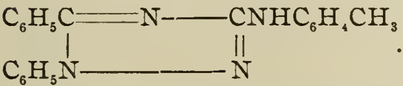


$$C_6H_5CON{=}C\left\langle\begin{matrix}NHC_6H_4CH_3\\ OC_2H_5\end{matrix}\right.$$

.—From paratoluidine and benzoylimidodiethylthiocarbonate. After standing two days the pseudourea crystallized in beautiful prisms. It separated from an alcoholic solution as an oil, and then crystallized in the form of long needles. It melted at 77° to 78°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.93	10.4

1,5-Diphenyl-3-paratolylaminotriazole,



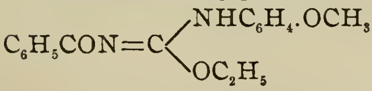
$$\begin{matrix}C_6H_5C & = & N- & CNHC_6H_4CH_3\\ | & & & \|\\ C_6H_5N & - & - & N\end{matrix}$$

.—This triazole was obtained by heating benzoylpseudoethylparatolylurea with phenylhydrazine. It crystallized from alcohol in minute, prismatic crystals, and melted at 227° to 228°. A nitrogen determination gave :

	Calculated for $C_{21}H_{18}N_4$.	Found.
N	17.17	17.07

This same triazole was first obtained by treating benzoylparatolylthiolethylpseudothiourea with phenylhydrazine.[1] Its structure was definitely established in a later paper by Wheeler and Beardsley.[2]

Benzoylpseudoethylparaanisylurea,



$$C_6H_5CON{=}C\left\langle\begin{matrix}NHC_6H_4.OCH_3\\ OC_2H_5\end{matrix}\right.$$

. — From paraanisidine and benzoylimidodiethylthiocarbonate. After standing for about one week the pseudourea was finally obtained in a crystalline form. It crystallized from alcohol in long, slender prisms, and melted at 66° to 67°. A nitrogen determination gave :

	Calculated for $C_{17}H_{18}O_3N_2$.	Found.
N	9.4	9.9

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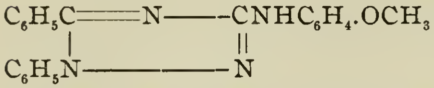
[1] Wheeler and Johnson : This Journal, **26**, 414.

[2] *Loc. cit.*

1,5-Diphenyl-3-p-anisylaminotriazole,

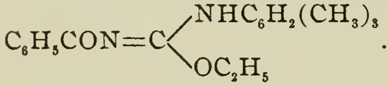


$$\begin{array}{lcl} C_6H_5C & {=\!=\!=}N{-\!-\!-} & CNHC_6H_4.OCH_3 \\ \quad | & & \quad \| \\ C_6H_5N & {-\!-\!-\!-\!-\!-\!-} & N \end{array}$$

.—From benzoylpseudoethyl-*p*-anisylurea and phenylhydrazine. It crystallized from alcohol in rosettes of slender prisms, melting at 224° to 225°. A nitrogen determination gave:

	Calculated for $C_{21}H_{18}ON_4$.	Found.
N	16.3	15.7

Benzoylpseudoethylpseudocumylurea,



$$C_6H_5CON{=}C\Big\langle\begin{array}{l} NHC_6H_2(CH_3)_3 \\ OC_2H_5 \end{array}$$

.—From pseudocumidine and benzoylimidodiethylthiocarbonate. After standing two days the pseudourea crystallized in magnificent prisms. It crystallized from alcohol in prisms and melted at 79° to 80°. A nitrogen determination gave:

	Calculated for $C_{19}H_{22}O_2N_2$.	Found.
N	9.03	9.03

Action of Benzoyl Rhodanide on Phenylhydrazine.

Eight grams of benzoyl rhodanide were dissolved in anhydrous ether and 5.3 grams of phenylhydrazine, mixed with ether, were slowly added through a dropping-funnel. A reaction took place at once and a beautiful, white, crystalline product separated from the ethereal solution. It crystallized from alcohol in the form of needles and prisms, and melted from 130° to 150°. The material behaved in every respect like a mixture.

The writer finally succeeded in purifying the material by repeated recrystallizations from alcohol. One product was isolated which was extremely soluble in alcohol and benzene. It separated in the form of needles and melted at 248°. It agreed in all its properties with 1,3-diphenyl-5-mercaptotriazole. Mixed with this triazole was another derivative which was somewhat less soluble in alcohol. By repeatedly crystallizing from alcohol it was obtained in a pure state and melted constant at 187°. It had all the properties of 1,5-diphenyl-3-mercaptotriazole. When mixed with this triazole the melting-point was not lowered.

The alcoholic mother-liquors from the above crystallizations were combined and allowed to stand at ordinary temperature. After about twelve hours a large amount of crystalline material had separated. It crystallized from alcohol in prisms and melted at 136°. When this compound was mixed with benzoylphenylthiosemicarbazide (m. p. 136°) the melting-point was not lowered.

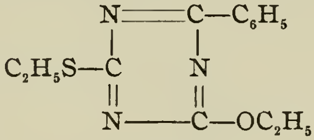
Acetone Derivative of a-Benzoyl-b-phenylthiosemicarbazide, $C_6H_5CONH.CSN(C_6H_5)N{=}C(CH_3)_2$.—This compound was prepared by mixing in anhydrous ether molecular proportions of benzoyl rhodanide and acetonephenylhydrazone. The ethereal solution was heated in the water-bath for about twenty minutes and then the ether was evaporated in a vacuum. The semicarbazide separated on the sides of the dish in the form of balls of minute prisms. It crystallized from alcohol in prisms and melted at 136°. A nitrogen determination gave:

	Calculated for $C_{17}H_{17}ON_3S$.	Found.
N	13.50	13.25

When some of this semicarbazide was treated with hydrochloric acid it was immediately converted into 1,3-diphenyl-5-mercaptotriazole melting at 248°. This same transformation takes place on long boiling with water. Several attempts were made to isolate the intermediate *a*-benzoyl-*b*-phenylthiosemicarbazide by more mild hydrolysis, but mixtures were obtained of the triazole and unaltered semicarbazide.

Condensation of Pseudoethylthiourea with Benzoylimidodiethylthiocarbonate.

Pseudoethylthiourea hydrobromide, $NH_2.C(SC_2H_5){=}NH.HBr$, was dissolved in alcohol and combined with a molecular proportion of sodium ethylate. To this alcoholic solution of the free pseudothiourea was then added a molecular proportion of benzoylimidodiethylthiocarbonate. At first there was no apparent reaction, but after standing about one hour mercaptan began to be given off freely. The mixture was allowed to stand at room temperature for about five days, when the excess of alcohol was evaporated on the steam-bath. We obtained a thick oil mixed with sodium bromide. The oil was taken up with ether to remove the sodium bromide, the ethereal solution dried over calcium chloride, and then the excess of ether evaporated in a vacuum. A beautiful crystalline deposit remained which showed signs of melting at 38°, and then melted to a turbid oil at 42° to 44°. The substance was extremely soluble in all the ordinary solvents. It crystallized from ligroin in prismatic crystals associated with some needles. When pure it crystallized from ligroin in well developed prisms, and melted at 47° to 48°. It was exceedingly stable, and after boiling with acids and alkalies it melted constantly at 47° to 48°. A nitrogen determination agreed with the calculated for ethylmercaptoethoxyphenyl-1,3,5-triazine,



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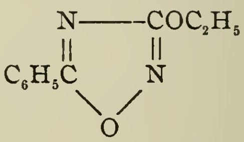
	Calculated for $C_{13}H_{15}ON_3S$.	Found.
N	16.09	16.41

α'-Phenyl-β-ethoxyfuro-α,β'-diazole,

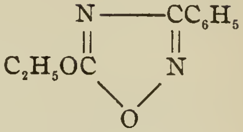


,

was obtained when an alcoholic solution of free hydroxylamine was united with a molecular proportion of benzoylimidodiethylthiocarbonate. Much heat was evolved and mercaptan was given off at once. After standing about eight hours the excess of alcohol was evaporated on the steam-bath. A beautiful crystalline deposit was formed, which was extremely soluble in ligroin, benzene, and ether. It crystallized from alcohol in stout prisms, and melted at 47° to 48°. A nitrogen determination gave :

	Calculated for $C_{10}H_{10}O_2N_2$.	Found.
N	14.72	15.2

α'-Ethoxy-β-phenylfuro-α,β'-diazole,



.—This derivative has been described by Falck,[1] but he represents it as having the alkyl group joined to nitrogen instead of oxygen. We have made it by allowing ethyl iodide to act on the silver salt of α'-oxy-β-phenylfuro-α,β'-diazole[1] at ordinary temperature. It was obtained as an oil, which was finally made to solidify by washing with a little dilute sodium hydroxide solution. It crystallized from a mixture of benzene and ligroin in colorless needles, and melted sharply at 36°. It agreed in all its properties with Falck's description. A nitrogen determination gave:

	Calculated for $C_{10}H_{10}O_2N_2$.	Found.
N	14.72	14.77

Benzoylisocyanchloride, $C_6H_5CONCCl_2$.—This chloride was made by leading dry chlorine gas into a chloroform solution of benzoyl rhodanide. The reaction was apparently very smooth, and could be safely accelerated by gently warming the chloroform solution on the steam-bath while passing in the gas. The chloroform solution gradually changed in color, finally becoming dark-red, when the reaction was assumed complete. The mixture was distilled under diminished pressure. After removing the excess of chloroform and sulphur chloride the bulk of the remaining oil distilled between 140° to 148° at 31 to 32 mm. pressure. A fraction boiling constantly at 146° to 148° at 31 mm. was reserved for analysis. A chlorine determination gave:

	Calculated for $C_8H_5ONCl_2$.	Found.
Cl	35.14	35.11

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[1] *Loc. cit.*

The oil is very sensitive towards moisture. It reacts with violence with alcohols and amines. The oil has a very penetrating odor and attacks the eyes.

New Haven, Conn., June 9, 1904.

ON THE FATE OF POTASSIUM MYRONATE IN THE ANIMAL ORGANISM AND ITS HYDROLYSIS BY THE FERMENTS OF THE LIVER.

By J. H. Kastle and Eloise Chesley McCaw.

Several years ago Kastle and Johnston made a comparative study of the distribution of emulsin and myrosin in the vegetable kingdom. It was found that the tissue and aqueous extracts of nearly every plant examined possessed the power to hydrolyze amygdalin, whereas myrosin seemed to be confined to a comparatively few orders of plants. It is known further that emulsin occurs in the animal organism. Such being the case, it occurred to us that it might prove of interest to study the fate of potassium myronate in the animal organism and to determine whether this glucoside could be hydrolyzed by ferments of animal origin.

Accordingly, 5 cc. of a solution of pure potassium myronate, containing 0.5 gram of the glucoside, were injected subcutaneously into a young Belgian hare, of about 1 kilogram weight. Immediately after the injection the animal was placed in a cage, so arranged that the urine could be collected. The animal received no food of any kind during the period of experimentation. No ill effects resulted from the injection of this quantity of the glucoside. In about three and one-half hours after the injection the animal passed urine, which was collected and tested for potassium myronate in the following manner. Four tubes were prepared as follows:

1. Contained 2 cc. of the urine, 2 cc. of an extract of white mustard-seed, the activity of which towards potassium myronate had been previously tested, and which contained 1 per cent of sodium fluoride as antiseptic.

2. Contained 2 cc. of the urine and 2 cc. of the extract of white mustard-seed, without antiseptic.

3. Contained 2 cc. of the urine and 2 cc. of the extract of white mustard, which had been previously boiled, and no antiseptic.

4. Contained 2 cc. of water and 2 cc. of the extract of white mustard. These tubes were then kept in a water-bath at 40° C. for several hours. In tubes 1 and 2 the odor of mustard-oil was distinctly perceptible in three hours, whereas in tubes 3 and 4 the odor of mustard-oil failed to develop even after a much longer interval. The urine failed to reduce Fehling's solution, whereas after standing for some time with the active extract of white mustard-seed it gave an abundant reduction.

These results go to show that when injected subcutaneously some of the potassium myronate at least passes unchanged into the urine, and that like the majority, if not all, of the complex carbohydrates and glucosides it is not directly assimilable from the blood.

The attempt was then made to determine whether the glucoside could be assimilated by the animal, if administered by the mouth. Accordingly, on April 13th, the rabbit was given a breakfast of bread, and 2 cc. of a solution of potassium myronate, containing 0.5 gram of the glucoside, was administered by the mouth. Almost immediately the animal passed into a lethargic condition and continued to lose weight during the interval of the experiment, which lasted for several days. Ten minutes after the administration of the myronate the animal passed urine. This was tested for potassium myronate, by the method above described, with negative results. The animal passed urine a second time at the end of twenty-four hours. This specimen was also tested for myronate in the usual manner but also with entirely negative results. It was observed further that the urine did not reduce Fehling's solution either before or after treatment with the active extract of white mustard-seed. Still other specimens of urine obtained at later intervals were examined for potassium myronate with negative results. It would seem, therefore, that when taken by the mouth the potassium myronate is assimilated in the animal organism, and that it is completely hydrolyzed at some point in the alimentary system.

The Hydrolysis of Potassium Myronate by the Ferments of the Liver.

The fact that the liver contains so many ferments and that it plays such an important part in processes of digestion and assimilation naturally suggested that possibly aqueous extracts of the liver might be found capable of hydrolyzing potassium myronate. In order to determine whether aqueous extracts of the liver could effect the hydrolysis of this compound, the following experiments were carried out: Five grams of the liver of the hog were thoroughly macerated by grinding in a mortar with fragments of glass. The mass was then intimately mixed with 50 cc. of water and strained through a muslin cloth. The conduct of this extract towards potassium myronate was then tested in the following manner:

Tubes were prepared containing equal amounts of a 1 per cent solution of potassium myronate and 5 cc. of the active and boiled extract of the liver, using in one experiment sodium fluoride and in another chloral as an antiseptic. The tubes were then heated to 40° C. in the water-bath for several hours. Those containing the active extract gave the odor of oil of mustard after several hours, whereas the control experiments gave no odor of this compound. These preliminary experiments seemed to indicate that the liver contains a ferment capable of hydrolyzing potassium myronate. On the other hand, the fact that such a small amount of the compound was hydrolyzed under these conditions would seem to show either that the liver contains only very small amounts of myrosin, or that the ferment could not be extracted from the liver cells by the method here employed. In order, therefore, to throw further light upon the subject the following experiments were carried out, using beef liver: One gram of liver was thoroughly macerated and intimately mixed in the porcelain mortar with 0.1 gram of potassium myronate. Five cc. of water were then rubbed into the mass and a small amount of sodium fluoride added. The mixture was then placed in a test-tube and tightly corked. A second tube was prepared similar to the first, except that toluene was used as the antiseptic. These, together with a control experiment in which the liver employed had previously been heated to boiling, completed the series. The three tubes were then heated on the water-bath at 40° C. for three hours. The odor of mustard oil was very strong in the first tube and its contents were thickly coagulated, doubtless as the result of the action of the acid potassium sulphate resulting from the hydrolysis of the myronate. The odor of oil of mustard was fainter in the second tube, although still readily perceptible, and the clear filtrate therefrom was found to reduce Fehling's solution. The boiled control gave no odor of oil of mustard, and the filtrate therefrom did not reduce Fehling's solution. The results of these experiments left no room for doubt that the liver of the beef is capable of hydrolyzing potassium myronate. Similar experiments were carried out using the liver of other animals and other animal tissues with the following results :

Tissue employed.	Duration of experiment.	Results.
Liver of hog	24 hours	+
Pancreas of hog	"	—
Muscle of hog	"	—
Spleen of hog	"	—
Kidney of hog	"	—
Lung of hog	"	—
Mucous membrane of small intestine of hog	"	—
Liver of beef	3 hours	+
Liver of dog	21 hours	+
Spleen of dog	"	—
Kidney of dog	"	—
Mucous membrane of small intestine of dog	"	—
Liver of cat	2 hours	+
Liver of hen	24 hours	+
Liver of rabbit	1 hour	+
Liver of rat	24 hours	+
Liver of mouse	"	+
Liver of sheep	20 hours	+
Liver of frog	24 hours	+
Liver of fish	"	—

In the above table the sign + indicates that the odor of oil of mustard developed in the time indicated, whereas the sign — indicates that no odor of oil of mustard was perceptible.

It is evident from these results that the liver of all animals thus far investigated, with the exception of that of the fish, contains a ferment capable of effecting the hydrolysis of potassium myronate. It is interesting to note further that the liver seems to be the only source of animal myrosin.

Our results would seem to warrant the further conclusion that, like other complex carbohydrates and glucosides, potassium myronate is not directly assimilable from the blood, but that when administered by the mouth it is assimilated, probably through the agency of the liver. In certain of our experiments it has been observed that the solution reduced Fehling's solution before the odor of mustard was noticeable. This would seem to indicate that the hydrolysis of this glucoside by animal myrosin probably takes place in two stages, the first of which results in the splitting off of glucose, the second in the further breaking-down of the residue into oil of mustard and potassium acid sulphate.

STATE COLLEGE OF KENTUCKY.
LEXINGTON, June, 1904.

ON THE OXIDATION OF SULPHOCYANIC ACID AND ITS SALTS BY HYDROGEN PEROXIDE.

BY J. H. KASTLE AND CLAUDE ROBERT SMITH.

In the course of their study of the decomposition of hydrogen peroxide, Kastle and Loevenhart[1] observed that ammonium sulphocyanate is readily oxidized by hydrogen peroxide even in the cold and even in the absence of oxygen carriers, with the production of acid ammonium sulphate and hydrocyanic acid. It therefore occurred to one of us (Kastle) that it might prove of interest to study this oxidation somewhat more at length. A few preliminary experiments indicated that the reaction would lend itself to quantitative measurements. These were carried out by measuring the increase in the acidity of the solution. Since, however, it was desired to employ phenolphthalein as the indicator, ammonium sulphocyanate could not be used. With the metallic sulphocyanates, however, and with sulphocyanic acid itself, satisfactory measurements have been made by means of this indicator. Generally, the experiments were carried out in large test-tubes, in a total volume of 25 cc. In most of the experiments the total volume of 25 cc. consisted of 10 cc. of N/10 sulphocyanic acid or the sulphocyanate, 6 cc. of M/2 hydrogen peroxide, the theoretical amount, and 9 cc. of water.

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[1] This JOURNAL, **29**, 397, 563 (1903).

The hydrogen peroxide was usually added last; the time of its addition served to mark the beginning of the experiment. At the end of certain intervals 5 cc. of the mixture were pipetted out and titrated with N/25 potassium hydroxide, using phenolphthalein as the indicator. The effect of various oxygen carriers on the progress of the oxidation, the effect of increasing amounts of hydrogen peroxide, the effect of temperature, and, finally, the order and velocity of the reaction have all been investigated. The results of these observations are given in the following pages.

On the Effect of Various Oxygen Carriers on the Progress of the Oxidation.

The influence of small amounts of the following substances on the progress of the oxidation has been studied: Manganese chloride, manganese dioxide, silver nitrate, potassium chloride, potassium bromide, potassium iodide, copper sulphate, copper nitrate, copper acetate, ferrous sulphate, mercuric chloride, and platinum black. Three series of experiments were carried out, one with potassium sulphocyanate, one with barium sulphocyanate, and one with sulphocyanic acid. In the experiments with platinum black and manganese dioxide 0.1 gram of each of these substances was employed. Equivalent quantities of the other substances were used, *viz.*, 2 cc. of a M/50 solution of each. The results of these experiments, together with all other necessary data, are given in Tables I., II., and III.

Table I.

Substances employed: 10 cc. N/10 potassium sulphocyanate; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9. cc. water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required.

Time in minutes.	Water.	Manganese chloride.	Silver nitrate.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Nickel sulphate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	0.70	0.70	0.60	0.70	0.60	0.70	1.65	2.05	0.85	0.75	1.00	1.00	3.30	0.70	0.20	0.60
180	1.05	1.10	1.00	0.95	0.90	1.10	2.05	2.50	1.50	1.2	1.30	1.35	3.50	1.25	0.25	1.00
270	1.35	1.45	1.30	1.35	1.35	1.45	2.25	3.00	1.60	1.55	1.50	1.70	3.50	1.65	0.25	1.30
360	1.55	1.65	1.55	1.55	1.65	1.65	2.30	3.05	1.70	1.85	1.80	1.90	3.60	2.10	0.25	1.65
1360	2.30	2.45	2.30	2.30	2.40	2.20	2.55	3.25	2.40	2.30	2.45	2.55	3.60	3.00	0.25	2.15

Per cent of potassium sulphocyanate oxidized.

Time in minutes.	Water.	Manganese chloride.	Silver nitrate.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Nickel sulphate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	14.0	14.0	12.0	14.0	12.0	14.0	33.0	41.0	17.0	15.0	20.0	20.0	64.0	14.0	4.0	12.0
180	21.0	22.0	20.0	19.0	18.0	22.0	41.0	50.0	30.0	24.0	26.0	27.0	70.0	25.0	5.0	20.0
270	27.0	29.0	26.0	27.0	27.0	29.0	45.0	60.0	32.0	31.0	30.0	34.0	70.0	33.0	5.0	26.0
360	31.0	33.0	31.0	31.0	33.0	33.0	46.0	61.0	34.0	37.0	36.0	38.0	72.0	42.0	5.0	33.0
1360	46.0	49.0	46.0	46.0	48.0	44.0	51.0	65.0	48.0	46.0	49.0	51.0	72.0	60.0	5.0	43.0

Table II.

Substances employed: 10 cc. N/10 barium sulphocyanate; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9 cc. of water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required.

Time in minutes.	Water.	Manganese chloride.	Chrome alum.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Nickel sulphate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	0.35	0.60	1.10	0.40	0.45	..	1.50	1.85	0.50	0.75	0.75	..	3.40	0.50	0.10	0.55
180	0.80	1.50	1.75	0.90	0.85	..	1.65	2.75	1.15	1.10	1.45	..	3.30	1.05	0.10	0.95
270	1.30	2.60	1.85	1.10	1.00	..	1.90	2.90	1.90	1.90	1.65	..	3.35	1.35	0.10	1.20
1360	1.90	2.70	2.50	1.85	1.85	..	2.15	2.90	2.00	2.00	2.60	..	3.30	2.00	0.10	1.75
Per cent of barium sulphocyanate oxidized.																
90	7.0	12.0	22.0	8.0	9.0	..	30.0	39.0	10.0	15.0	15.0	..	68.0	10.0	2.0	11.0
180	16.0	30.0	35.0	18.0	17.0	..	33.0	55.0	23.0	22.0	29.0	..	66.0	21.0	2.0	19.0
270	26.0	52.0	37.0	22.0	20.0	..	38.0	58.0	38.0	38.0	33.0	..	67.0	27.0	2.0	24.0
1360	38.0	54.0	50.0	37.0	37.0	..	43.0	58.0	40.0	40.0	52.0	..	66.0	40.0	2.0	35.0

Table III.

Substances employed: 10 cc. N/10 sulphocyanic acid; 2 cc. M/50 of the substance tested; 6 cc. M/2 hydrogen peroxide; 7 or 9 cc. of water. Total volume of solution = 25 cc. Temperature, 20° C.

Cc. N/25 potassium hydroxide required after deducting initial acidity of solution.

Time in minutes.	Water.	Manganese chloride.	Chrome alum.	Potassium chloride.	Potassium bromide.	Potassium iodide.	Copper nitrate.	Copper sulphate.	Nickel nitrate.	Cobalt nitrate.	Cobalt sulphate.	Ferrous sulphate.	Mercuric chloride.	Manganese dioxide.	Platinum black.
90	1.85	2.05	3.50	2.00	2.05	2.00	3.20	3.60	2.60	2.70	2.70	3.60	2.35	2.00	2.50
180	2.80	2.60	3.80	2.75	2.75	2.90	3.70	3.80	3.35	3.40	3.40	3.70	3.10	2.85	3.00
270	3.35	3.25	3.85	3.30	3.35	3.30	3.90	4.00	3.50	3.60	3.60	3.75	3.30	3.35	3.15
1140	3.45	3.35	3.95	3.45	3.40	3.50	3.90	4.10	3.65	4.00	4.00	3.75	3.70	3.35	3.25
Per cent of sulphocyanic acid oxidized.															
90	37.0	41.0	70.0	40.0	41.0	40.0	64.0	72.0	52.0	54.0	54.0	72.0	47.0	40.0	50.0
180	56.0	52.0	76.0	55.0	55.0	58.0	74.0	76.0	67.0	68.0	68.0	74.0	62.0	57.0	60.0
270	67.0	65.0	77.0	66.0	67.0	66.0	78.0	80.0	70.0	72.0	72.0	75.0	66.0	67.0	63.0
1140	69.0	67.0	79.0	69.0	68.0	70.0	78.0	82.0	73.0	80.0	80.0	75.0	74.0	67.0	65.0

It is evident from these results that both in the presence of oxygen carriers and alone sulphocyanic acid is more rapidly oxidized by hydrogen peroxide than either of its salts. Secondly, that the oxidation both of the acid and the two sulphocyanates here employed is greatly accelerated by various substances, notably by those which have been found to effect the decomposition of hydrogen peroxide. Prominent among these are chrome alum, copper sulphate and nitrate, and ferrous sulphate. The salts of nickel and cobalt also accelerated the oxidation of the sulphocyanic acid, and to about the same extent each, whereas they exercised but little influence on the oxidation of the salts. Still another point of interest is that platinum black, manganese dioxide, and potassium iodide, all of which have been found to accelerate the oxidation of certain other substances by hydrogen peroxide, are in this case practically without influence on the rate of oxidation.

Determination of the Order and Velocity of the Reaction.

The oxidation of sulphocyanic acid by hydrogen peroxide is probably represented by the following equation:

$$HCNS + 3H_2O_2 = HCN + H_2SO_4 + 2H_2O.$$

If such is the case, the reaction in question is apparently of the fourth order. As but few reactions of high molecular order have ever been experimentally studied it occurred to us that it might prove of interest to determine the order of this reaction and also to determine the velocity of the reaction under different conditions.

Accordingly the order of the reaction was determined by van 't Hoff's method, as follows: Two flasks, A and B, of 50 cc. and 100 cc. capacity, respectively, were prepared thus: A received 20 cc. N/10 sulphocyanic acid, 12 cc. M/2 hydrogen peroxide, and 18 cc. of water; B received the same amount of acid and peroxide, but the water added to it was 68 cc. These two flasks contained, therefore, the same amounts of reacting substances but in different concentrations, the concentration of one being twice that of the other, the unit of volume being 50 cc. These were allowed to remain for thirty minutes at ordinary temperature, care being taken that both were under the same conditions. At the end of this time 10 cc. were pipetted out from the 50 cc. flask and titrated with N/25 potassium hydroxide. It required 14.15 cc., subtracting the initial acidity, equivalent to 10.12 cc. of N/25 potassium hydroxide; the amount of acid formed was equal to 4.03 cc., and the total acidity five times that amount; namely, 20.15 cc. We may tabulate these results, therefore, as follows:

Time in minutes.	Concentration.
0	50.00
30	29.85
Mean concentration,	39.925

Twenty cc. from the second flask, at the end of thirty minutes, required 11.50 cc. N/25 potassium hydroxide, that is, the acid formed was equivalent to 1.38 of N/25 potassium hydroxide, and hence the total acid generated was equivalent to five times that amount; namely, 6.9 cc.

Hence in the unit of volume at the second concentration the acid formed was equivalent to 3.45 cc. N/25 potassium hydroxide. These results, therefore, may be tabulated as follows:

Time in minutes.	Concentration.
0	25.00
30	21.65
Mean concentration,	23.275

Substituting these several values in van 't Hoff's equation, we arrive at the number representing the order of the reaction under consideration:

$$n = \frac{\log \frac{(dC_1}{(dt} : \frac{dC_2)}{dt)}}{\log (C_1 : C_2)} = \log \frac{\frac{dC_1}{dt} - \log \frac{dC_2}{dt}}{\log C_1 - \log C_2}.$$

$$\frac{dC_1}{dt} = \frac{50 - 29.85}{30} = 0.6716; \quad C_1 = 39.925.$$

$$\frac{dC_2}{dt} = \frac{25 - 21.55}{30} = 0.115; \quad C_2 = 23.275.$$

$\log^e 0.6716 = -0.3981$; $\log_e 0.115 = -8.21626$.

$\log_e 39.925 = 3.6870$; $\log_e 23.275 = 3.1474$.

Therefore,

$$n = \frac{-0.3981 - (-2.1626)}{3.6870 - 3.1474} = \frac{1.7645}{0.5396} = 3.27.$$

It would seem reasonable to conclude, therefore, that the change under investigation is one of the third order. Looked at from this standpoint, the oxidation of sulphocyanic acid by hydrogen peroxide probably takes place in two entirely distinct and independent stages, the first of which leads to the production of hydrocyanic acid and sulphur dioxide, the second involving the further oxidation of the sulphur dioxide to sulphuric acid. Thus we would have:

$$HCNS + 2H_2O_2 = HCN + 2H_2O + SO_2 ;$$

and $$SO_2 + H_2O_2 = H_2SO_4.$$

It is known that the oxidation of aqueous solutions of sulphur dioxide by hydrogen peroxide takes place with great rapidity at ordinary temperatures. Hence the amount of sulphuric acid formed in a given time would depend entirely on the amount of sulphur dioxide produced in the first phase of the oxidation. The first phase of the oxidation, however, is clearly a trimolecular process. These facts are in keeping with all that is generally known concerning the conduct of sulphur and its compounds on oxidation, *viz.*, that the formation of sulphur dioxide always marks the first phase of such processes.

With the view of determining the velocity constant of the reaction the following experiments were carried out:

Two flasks, A and B, were prepared, each containing 40 cc. of N/10 sulphocyanic acid, 24 cc. of M/2 hydrogen peroxide, and 36 cc. of water. These flasks were allowed to stand at room temperature, 17°.5 C. At the end of certain intervals 20 cc. of the mixture were withdrawn from the flask by means of a pipette and titrated with N/25 potassium hydroxide. After making the necessary allowance for the initial acidity of the mixture the following results were obtained:

Time in minutes.	Volume N/25 KOH required. A. cc.	B. cc.	C. A.	B.
30	3.69	3.79	0.0000009260	0.0000009260
60	5.99	5.99	0.0000009642	0.0000009642
90	7.79	7.94	0.0000010537	0.0000010970
120	8.99	9.09	0.0000010901	0.0000011940
150	10.09	10.24	0.0000011073	0.0000011519

The several values of C are calculated according to the equation for a reaction of the third order, $C = \frac{1}{x} \cdot \frac{x(2A-x)}{2A(A-x)}$.

It will be observed that in this series of experiments the velocity of the reaction slightly increases as the reaction proceeds. It was thought perhaps that this slight increase might be due to a slight rise of temperature during the progress of the experiment. It seemed desirable, therefore, to conduct a series of experiments at a perfectly constant temperature. Accordingly, two flasks were prepared, each containing 40 cc. N/10 sulphocyanic acid, 24 cc. M/2 hydrogen peroxide, and 36 cc. of water. During the interval of experimentation the flasks were kept in a bath of cracked ice. At the end of certain intervals 20 cc. of the solution were withdrawn from the flask by means of a pipette and titrated with N/25 potassium hydroxide. The results of this series of measurements are given in the table below, correction being made for the initial acidity of the solution.

Time in minutes.	Volume N/25 KOH required. A. cc.	B. cc.	C. A.	B.
30	1.24	1.24	0.0000002494	0.0000002494
60	2.19	2.19	0.0000002389	0.0000002389
90	3.09	3.09	0.0000002441	0.0000002441
120	3.99	3.99	0.0000002581	0.0000002581
			Average,	0.0000002476

A similar series of experiments with potassium sulphocyanate at 17°.5 C. gave the following results :

Time in minutes.	Volume N/25 KOH required.		C.	
	A.	B.	A.	B.
	cc.	cc.		
30	0.61	0.61	0.0000001065	0.0000001065
60	1.11	1.11	0.0000001008	0.0000001008
90	1.61	1.61	0.0000001015	0.0000001015
120	2.06	2.11	0.0000001012	0.0000001042
150	2.51	2.51	0.0000001021	0.0000001021
		Average,	0.0000001024	0.0000001030

We see thus that in the process under consideration it is possible to obtain fairly constant values for the coefficient of velocity of a reaction of the third order.

Finally, it has been observed that a rise of temperature of 10° C. nearly doubles the velocity of the reaction. That such is the case may be seen from the following:

Time in minutes.	Velocity constant at 0° C.	Velocity constant at 10° C.
30	0.0000002494	0.0000004649
60	0.0000002389	0.0000004633
Average,	0.00000024415	0.0000004641
Ratio of velocities at T and (T + 10)		1.90

This is in accord with the generalizations of van 't Hoff respecting the influence of temperature on chemical change.

State College of Kentucky,
Lexington, June, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VII.—THE PREPARATION OF AROMATIC NITROSO COMPOUNDS.

By Frederick J. Alway.

Up to the present time there has been developed no method of general application for the preparation of those aromatic nitroso compounds in which the nitrogen is attached to a carbon atom and of which nitrosobenzene is the simplest example. While, within recent years, a large number of the nitroso compounds has been prepared, the fact that such comparatively simple compounds as *m*-nitrosobenzoic acid and *p*-nitrosobenzoic acid have not hitherto been obtained, indicates the want of some general method of procedure. Nearly all the nitroso compounds at present known are readily volatile with steam and, so, are easily separated from other compounds formed at the same time. The method that has been used in preparing most of the members of this class is that of Bamberger,[1] which consists in the oxidation of the β-alphylhydroxylamines obtained by the action of zinc dust and an ammonium salt solution upon the corresponding nitro compounds. When the resulting substance was not the pure nitroso compound, distillation with steam was used. The oxidation of amido compounds by means of Caro's reagent[2] has also been used by Bamberger[3] and to a limited extent by others[4] in the preparation of the same class of substances. The bright-green color of all nitroso compounds in solution and the characteristic odor of most of them made them easy of recognition. *o*-Nitrosobenzoic acid, which is not volatile with steam, has been prepared by E. Fischer[5] by the oxidation of the phenyloxindol obtained from benzoinoxime, using potassium permanganate as an oxidizing agent, and by Ciamician and Silber[6] by allowing solutions of *o*-nitrobenzaldehyde to stand exposed to the sunlight. The reaction in the latter case takes place according to the following equation :

$$O_2N.C_6H_4.CHO \longrightarrow ON.C_6H_4.CO.OH.$$

Similarly, Sachs and Kempf[7] have obtained *p*-chlor-*o*-nitrosobenzoic acid from the corresponding *p*-chlor-*o*-nitrobenzaldehyde.

In a former publication[8] I have pointed out that *p*-nitrosobenzaldehyde, while readily volatile with steam when freshly prepared by oxidizing *p*-hydroxylaminobenzaldehyde, is not volatile after it has been preserved for some time. It can, however, be changed back into the volatile form by fusion or by solution in alcohol or in acetic acid. Later,[1] I found that when zinc dust was added to the alcoholic solution of *p*-nitrobenzaldehyde containing acetic acid the zinc dissolved rapidly until the amount approximately corresponding to the equation

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[1] Ber. d. chem. Ges., **28**, 245, 1218 (1895).
[2] Chem. Centrbl., II., 190 (1899).
[3] Ber. d. chem. Ges., **36**, 3803 (1903).
[4] *Ibid.*, **35**, 3034 (1902).
[5] *Ibid.*, **29**, 2064 (1896).
[6] *Ibid.*, **34**, 2040 (1901) ; **35**, 1080, 1897, 3596 (1902).
[7] *Ibid.*, **36**, 3302 (1903).
[8] J. Am. Chem. Soc., **24**, 1059 (1902).

$$O_2N.C_6H_4.CHO + 2Zn + 4C_2H_4O_2 = HO.NH.C_6H_4.CHO + H_2O + 2Zn(C_2H_3O_2)_2$$

had disappeared, the solution assuming an orange color. The further addition of zinc produced no change. Zinc and acetic acid acted similarly upon other nitro compounds, including the nitrobenzoic acids as well as those nitro compounds from which nitroso compounds had been prepared. While the reduction-products of the latter gave, upon oxidation and distillation with steam, green distillates, the former gave colorless distillates. As, in most cases, the nitroso compounds were more readily volatile with steam than the corresponding nitro compounds, and as the nitrobenzoic acids were not volatile with steam, an investigation of the possibility of preparing nitroso compounds from non-volatile nitro compounds was undertaken in this laboratory. With the exception of *o*-nitrobenzoic acid and *o*-nitrocinnamic acid, all the nitro compounds so far worked with have given nitroso compounds. Farther, as in the case of *p*-nitrosobenzaldehyde, *m*-nitrosobenzaldehyde, and the nitrosobenzoic esters the corresponding azoxy compounds were formed at the same time by the oxidation of the β-hydroxylamines, it seemed probable that the oxidation-product of the substances obtained by the action of zinc dust and acetic acid upon the nitro acids was chiefly a mixture of nitroso and azoxy acids. Following this hypothesis four non-volatile nitroso acids have been isolated in this laboratory, *viz.*, *m*-nitrosobenzoic acid, *p*-nitrosobenzoic acid, *m*-nitrosocinnamic acid, and *p*-nitrosocinnamic acid. The phenomena observed upon the oxidation of the *o*-hydroxylamino acids were quite different from those observed in the other cases. No attempt was made to isolate any of the hydroxylamino compounds except that obtained from *p*-nitrobenzaldehyde.[2]

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[1] Ber. d. chem. Ges., **36**, 793, 2303 (1903).

[2] J. Am. Chem. Soc., **24**, 1057 (1902).

The *m*- and *p*-nitrosobenzoic and the *m*- and *p*-nitrosocinnamic acids are not volatile with steam. They decompose without melting. *p*-Nitrosobenzoic acid and *p*-nitrosocinnamic acid pass more or less completely, on standing, into insoluble modifications. The latter dissolve, however, in hot sodium carbonate solution, from which they are precipitated by acids in a form soluble in ordinary solvents.

While all other nitroso compounds of this class are colorless or some shade of green or blue in the solid form, *p*-nitrosobenzoic acid and its esters, as well as *p*-nitrosocinnamic acid and its esters, *p*-nitrosobenzaldehyde and *p*-nitronitrosobenzene,[1] are yellow. All the yellow nitroso compounds, except the cinnamic series, form green solutions. The cinnamic compounds form yellowish-green or greenish-yellow solutions.

In view of the results already obtained, the following method is suggested as one likely to indicate the best means of obtaining any nitroso compound that has not hitherto been prepared: First, determine the volatility of the corresponding nitro compound. If it is volatile with steam reduce it in alcoholic solution by means of zinc dust and acetic acid. Treat the reduction-product with ferric chloride solution and subject the mixture at once to the action of steam. If the nitro compound is not volatile with steam proceed as above as far as the oxidation. Wash the oxidation-product well with water in order to remove as much as possible of the ferric chloride, as small quantities of ferric compounds hide the characteristic color of the nitroso compounds in solution. Extract the residue at once with a hot solvent. (Alcohol has proven the most satisfactory solvent in the reactions so far studied.) Repeated solution and reprecipitation may in some cases be found necessary in order to remove the ferric salts sufficiently to allow the characteristic color to appear. In some cases zinc dust and an ammonium salt solution may be found to give a better yield of the nitroso compound. Where it is preferable to prepare the nitroso compound from the amido compound the determination of the volatility of the nitro compound will indicate the method to be used in separating the nitroso from the accompanying azoxy compound. Bamberger and Hübner[1] have shown that the two form at the same time when the amido compounds are oxidized by Caro's reagent.

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[1] Ber. d. chem. Ges., **36**, 3809 (1903).

A brief notice regarding the preparation of *m*- and *p*-nitrosobenzoic acids has already been published elsewhere.[2] Some modifications of the methods there outlined have since been found desirable.

EXPERIMENTAL.

p-Nitrosobenzoic Acid, $ON.C_6H_4.COOH$.—Five grams of *p*-nitrobenzoic acid were dissolved, by the aid of heat, in ordinary alcohol. This solution was rapidly cooled to the temperature of the room so that any acid that separated out might be in a fine state of division. After adding 10 cc. of glacial acetic acid and shaking the mixture well, 5 grams of zinc dust were added in small portions, with constant agitation. The mixture became warm, the greater part of the zinc dissolved, and the solution assumed an orange color. The crude reduction-product was poured into a cold 10 per cent ferric chloride solution and the mixture warmed to 45°. A yellow, flocculent precipitate formed. This was filtered out and washed thoroughly on the filter with water to remove as much as possible of the adhering ferric compounds. The moist residue was boiled with ordinary alcohol and the green alcoholic solution filtered from the dark-colored residue. This extraction was repeated with fresh portions of alcohol until the filtrates ceased to be green. A gray, insoluble substance remained. When the oxidation-product was allowed to dry before treatment with hot alcohol the whole of it became insoluble. On standing, a yellow powder separated from the green solution.

0.2830 gram substance gave 23.7 cc. moist N at 14° and 730 mm.

	Calculated for $C_7H_5O_3N$.	Found.
N	9.3	9.4

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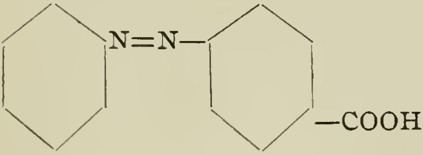
[1] Ber. d. chem. Ges., **36**, 3803 (1903).

[2] *Ibid.*, **37**, 333 (1904).

p-Nitrosobenzoic acid forms a yellow powder without distinct crystal form. It decomposes above 250° without melting. On drying, it becomes insoluble in ordinary solvents. A specimen that had been preserved five months was quite insoluble in boiling alcohol, acetic acid, and benzene; it dissolved in hot sodium carbonate solution with a yellowish-green color. This solution, when rendered acid, gave a yellow, amorphous precipitate, which, while still moist, dissolved in hot alcohol with a green color. *p*-Nitrosobenzoic acid dissolves in ammonia with a yellowish-green color. It is not volatile with steam. With aniline it condenses to benzene-*p*-azobenzoic acid.

Benzene-p-azobenzoic Acid, 

.—*p*-Nitrosobenzoic acid was treated with an excess of aniline dissolved in glacial acetic acid and the mixture heated to boiling until the *p*-nitrosobenzoic acid had entirely dissolved. The reddish-brown solution thus obtained was cooled and then treated with dilute nitric acid. A reddish-brown precipitate formed. This was filtered out and twice recrystallized from alcohol. The acid formed orange crystals melting at 240° (uncorr.). The same acid had previously been prepared by other methods.[1]

m-Nitrosobenzoic Acid, $ON.C_6H_4.COOH$.—Five grams of *m*-nitrobenzoic acid, dissolved in 50 cc. of ordinary alcohol, were treated with 10 cc. of glacial acetic acid and then with 5 grams of zinc dust. The last was added in small portions with constant shaking. The mixture became warm, most of the zinc dissolved, and a clear light-yellow solution was formed. The unchanged zinc was filtered out and the filtrate poured into a 10 per cent solution of ferric chloride. A yellow solid rose to the surface of the mixture on standing. This was filtered out, washed on the filter with water, and extracted with boiling alcohol, as described above in the case of the isomeric acid. There was thus obtained a brown solution, while a gray insoluble substance remained on the filter. The brown solution, when diluted with water and allowed to stand, gave a light-colored precipitate. The latter was washed with water repeatedly by decantation and finally on a suction-filter. On recrystallization from alcohol it formed a white solid without distinct crystal form.

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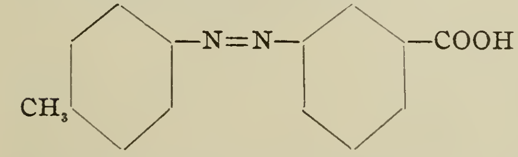
[1] Ber. d. chem. Ges., **19**, 3023 (1886); Ann. Chem. (Liebig), **303**, 384 (1881).

0.1092 gram substance gave 9.1 cc. moist N at 14° and 723 mm.

	Calculated for $C_7H_5O_3N$.	Found.
N	9.3	9.3

m-Nitrosobenzoic acid, when heated, blackens at 230° without melting. It is not volatile with steam. It forms green solutions. With *p*-toluidine it forms *p*-toluene-*m*-azobenzoic acid.

p-Toluene-m-azobenzoic Acid,



. — A mixture of *m*-nitrosobenzoic acid, *p*-toluidine, and glacial acetic acid was heated to boiling for five minutes. The brown solution thus obtained was cooled and treated with dilute nitric acid. A brown solid separated out. This was filtered out and recrystallized from alcohol several times. The acid forms orange crystals melting at 192° (uncorr.). Löb[1] has obtained the same compound by the electrolytic reduction of a mixture of *p*-nitrotoluene and *m*-nitrobenzoic acid.

The gray residues obtained by extracting the *p*- and *m*-nitrosobenzoic acids from the oxidation-products were soluble in ammonia. The ammoniacal solutions, when rendered acid by the addition of mineral acids, gave light-colored precipitates. When the latter were filtered out and dried they were found to be insoluble in ordinary solvents, and when heated they decomposed without melting. These properties, together with their method of formation, serve to identify them as the azoxy acids.[1]

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[1] Ber. d. chem. Ges., **31**, 2204 (1898).

o-Nitrobenzoic acid, when treated with zinc dust and acetic acid, gave a yellow solution. This reduction-product, when treated with ferric chloride solution, gave red or indigo-blue substances, according to the conditions of reaction. No nitroso compound was separated from these oxidation-products.

No attempt was made to isolate the hydroxylamino acids.

UNIVERSITY PLACE, NEBRASKA,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

VIII.—THE NITROSOCINNAMIC ACIDS AND ESTERS.

BY FREDERICK J. ALWAY AND WALTER D. BONNER.

The volatility of the nitroso compounds is, in most cases, only slightly greater than that of the corresponding nitro compounds. *m*-Nitrocinnamic acid and *p*-nitrocinnamic acid are not volatile with steam, but their ethyl and methyl esters are volatile, though with difficulty. We have found that the nitroso compounds are very similar in their behavior toward steam to these nitro compounds. This fact renders their purification very difficult and the yields of pure substance extremely small. The para compounds are yellow, like the *p*-nitrosobenzoic compounds. The ethyl and methyl esters of *p*-nitrosocinnamic acid exist also in an instable, green modification. While *m*-nitrosocinnamic acid is colorless, its ethyl ester forms green crystals. Attempts to obtain *o*-nitrosocinnamic acid were unsuccessful. Evidently the corresponding azoxycinnamic acids are formed together with the *m*- and *p*-nitrosocinnamic acids.

EXPERIMENTAL.

p-Nitrocinnamic Acid, $O_2N.C_6H_4.CH:CH.COOH$.—This compound was prepared by heating, for eight hours, a mixture of 30 grams acetic anhydride, 22 grams of *p*-nitrobenzaldehyde, and 10 grams of powdered anhydrous sodium acetate.

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[1] J. Chem. Soc. (London), **73**, 146; Ann. Chem. (Liebig), **196**, 18.

The flask containing this mixture was fitted with an air-condenser and heated in an oil-bath kept at a temperature of 180° by means of a thermoregulator. The reaction-product was distilled with steam until the odor of nitrotoluene could no longer be detected in the distillate. The crude *p*-nitrocinnamic acid was dissolved in sodium carbonate solution. After filtering this solution from any undissolved substance it was rendered acid by means of hydrochloric acid. The *p*-nitrocinnamic acid separated out in almost colorless, needle-shaped crystals. The yield was about 90 per cent of the theoretical amount.

p-Nitrosocinnamic Acid, $ON.C_6H_4.CH : CH.CO.OH$.—Two grams of finely divided *p*-nitrocinnamic acid were placed in a flask together with 4 cc. of glacial acetic acid and 50 cc. of alcohol. The contents of the flask were then well shaken and immediately treated with 2 grams of zinc dust. The mixture at once became green in color and warm. After ten minutes, during which the contents of the flask were kept well agitated, the unchanged zinc was filtered out and the clear, orange filtrate poured into a 10 per cent ferric chloride solution, which was kept at 40° to 60°. The yellow solid, that separated out, was filtered out, washed with water, and extracted with boiling alcohol, a brown, insoluble substance remaining on the filter. The alcoholic extract, which had a greenish-yellow color, deposited, on standing, a yellow solid. A further deposit was obtained by the addition of water to the filtrate from the first. The solid substance was brownish-yellow in color and a nitrogen determination showed that it was impure. The yield of crude acid was small and the loss attending each recrystallization was very large. After the third recrystallization from alcohol the substance was of a yellow color, with only a trace of brown. A nitrogen determination showed that it was still slightly impure.

0.2814 gram substance gave 19.2 cc. moist N at 23° and 730 mm.

	Calculated for $C_9H_7O_3N$.	Found.
N	7.9	7.4

By further recrystallization a small amount of the acid was obtained that had a pure yellow color, without a tint of brown. There was not enough of this pure acid, however, for an analysis.

p-Nitrosocinnamic acid forms a yellow powder of indistinctly crystalline form. It does not melt, but blackens when heated above 220°. When freshly prepared it is soluble in alcohol and in glacial acetic acid, giving yellowish-green or greenish-yellow solutions. After having been preserved in a dry state for several days a part of it was found to be insoluble in alcohol. This portion was found to dissolve readily in sodium carbonate solution with a yellowish-brown color. On acidifying this solution, a yellow precipitate was formed. The latter dissolved in hot alcohol with a greenish-yellow color.

Ethyl p-Nitrocinnamic Ester, $O_2N.C_6H_4.CH:CH.CO.OC_2H_5$.—This compound was prepared by heating 2 grams of *p*-nitrocinnamic acid with 20 cc. of absolute alcohol and 1 cc. of concentrated sulphuric acid, on the water-bath with return-condenser, for three hours. The reaction-mixture was cooled, treated with water, and then with an excess of sodium carbonate solution. The undissolved solid was filtered out and recrystallized from alcohol. The yield was almost quantitative. The ester crystallizes from alcohol in brown needles, melting at 137° (uncorr.). On being subjected to the action of steam the ester volatilizes slowly, collecting in the receiver as white needles, which melt at 141° to 142° (uncorr.). About 0.2 gram of ester was carried over by 1,000 grams of water vapor.

Ethyl p-Nitrosocinnamic Ester,
$ON.C_6H_4.CH:CH:CO.OC_2H_5$.—Five grams of finely divided ethyl *p*-nitrocinnamic ester were treated with 75 cc. of alcohol and 12 cc. of glacial acetic acid. Zinc dust was then added in small quantities, with constant agitation, until the zinc was no longer dissolved. The mixture was then of an orange color. After standing ten minutes the reduction-product was poured, with constant stirring, into a 10 per cent ferric chloride solution. When the mixture was warmed, a yel-

low solid separated out. The crude oxidation-product was distilled with steam, a greenish-yellow liquid collecting in the receiver, while a brown solid remained in the distilling-flask. On standing over night yellow crystals separated from the distillate. The yield of nitroso compound varied from 10 to 15 per cent of the theoretical amount. It was found wasteful to place the reduction-product of more than 2 grams of the nitro compound in the distilling-flask at one time. Prolonged contact with boiling water seems to change the nitroso compounds into azoxy compounds.[1] After one recrystallization from aqueous alcohol the ester was pure.

0.1202 gram substance gave 8.1 cc. moist N at 23° and 724 mm.

	Calculated for $C_{11}H_{11}O_3N$.	Found.
N	6.8	7.2

Ethyl *p*-nitrosocinnamic ester forms yellow needles, which melt at 72° to 73° to a green liquid. It forms greenish-yellow solutions in alcohol, benzene, and acetic acid. On one occasion distinctly green crystals of the ester were obtained, but before they were dried they had changed to the yellow form, melting at 72° to 73°.

Methyl p-Nitrocinnamic Ester, $O_2N.C_6H_4.CH : CH.CO.OCH_3$.—This compound was prepared from *p*-nitrocinnamic acid and methyl alcohol by the same method as the ethyl ester. The yield was about 90 per cent of the theoretical amount. Like the ethyl ester, it volatilized very slowly in a current of steam, collecting in the receiver in the form of colorless crystals, melting at 160° (uncorr.).

Methyl p-Nitrosocinnamic Ester, $ON.C_6H_4.CH : CH.CO.OCH_3$.—One gram of the nitro ester was dissolved in boiling alcohol and treated with 2 cc. of glacial acetic acid. The hot solution was cooled under the tap so that the nitro ester would be in a fine state of division. Zinc dust was added to the mixture until, on warming gently, the zinc ceased to dissolve. The mixture became first green, then brown, and lastly yellow. It was then poured into ferric chloride solution, which gave a yellow precipitate. On distilling the oxidation-product with steam a yellowish-green solution collected in the receiver while a brown solid remained in the distilling-flask. Lemon-yellow, needle-shaped crystals separated from the distillate. The melting-point of these crystals was not raised by recrystallization.

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[1] Ber. d. chem. Ges., **36**, 3806 (1903).

0.2040 gram substance gave 13.6 cc. moist N at 24° and 732 mm.

	Calculated for $C_{10}H_9O_3N$.	Found.
N	7.3	7.2

Methyl *p*-nitrosocinnamic ester forms lemon-yellow needles, melting at 111° to 112° (uncorr.) to a green liquid. The latter, on cooling, forms a green solid, which, on standing exposed to the sunlight a few days, changes to the yellow form. On several occasions green crystals collected in the condenser. After these had been dried in the dark they could be left exposed to the light for several days before passing into the yellow modification. When moist, green crystals were exposed to the sunlight they underwent the change within an hour. A specimen of the green form has been preserved in the dark for two months without showing any sign of change. The green crystals have the same melting-point as the yellow.

m-Nitrosocinnamic Acid, $ON.C_6H_4.CH : CH.CO.OH$.—Two grams of *m*-nitrocinnamic acid (Kahlbaum's preparation) were dissolved in 50 cc. of alcohol, treated with 4 cc. of glacial acetic acid, and then with 2 grams of zinc dust. The light-yellow solution thus obtained was filtered from the small amount of unchanged zinc. The filtrate, when poured into a 10 per cent ferric chloride solution, gave a flocculent, yellow precipitate. This was filtered out, washed well with water, and extracted with boiling alcohol. A brown solid remained undissolved. The green alcoholic solution, when treated with water and allowed to stand several hours, gave a flocculent white precipitate. The latter was filtered out and recrystallized from alcohol.

0.1722 gram substance gave 12.1 cc. moist N at 25° and 730 mm.

	Calculated for $C_9H_7O_3N$.	Found.
N	7.9	7.5

m-Nitrosocinnamic acid forms stellate groups of minute white needles, which turn slightly brown when allowed to stand exposed to the air in a moist condition. It forms green solutions and decomposes, without melting, at 230°.

Ethyl m-Nitrocinnamic Ester, $O_2N.C_6H_4.CH:CH.CO.OC_2H_5$.—This ester was prepared by boiling on the water-bath, for three hours, a mixture of 5 grams *m*-nitrocinnamic acid, 50 cc. ordinary alcohol, and 10 cc. concentrated sulphuric acid. The solution, after cooling, was diluted with water and the white solid so obtained washed on the filter with sodium carbonate solution. On recrystallizing from alcohol the ester was obtained in white needles, melting at 78° to 79° (uncorr.). It is slightly more volatile with steam than the isomeric para ester.

Ethyl m-Nitrosocinnamic Ester,
$ON.C_6H_4.CH:CH.CO.OC_2H_5$.—Five grams of ethyl *m*-nitrocinnamic ester, dissolved in alcohol, were treated with 10 cc. glacial acetic acid and 3 grams of zinc dust, the latter being added in small portions. As the zinc dissolved the solution became warm and assumed a brownish-yellow color. The reduction-product was poured into a 10 per cent ferric chloride solution, a solid separating out almost immediately. The crude oxidation-product was at once distilled with steam. After the alcohol had passed over, the distillate became green and a few green crystals collected in the condenser. On standing, bright green crystals separated from the green distillate. The filtrate from these was colorless. Recrystallization from alcohol did not raise the melting-point of the crystals.

0.1904 gram substance gave 12.1 cc. moist N at 20° and 724 mm.

	Calculated for $C_{10}H_{11}O_3N$.	Found.
N	6.8	6.9

Ethyl *m*-nitrosocinnamic ester forms bright-green, rhombic plates, readily soluble in alcohol, and melting at 65° to 66° (uncorr.). In solution and when melted it is green.

UNIVERSITY PLACE, NEBRASKA.,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

IX.—ON CERTAIN NITROGEN COMPOUNDS.

BY FREDERICK J. ALWAY AND REUBEN M. PINCKNEY.

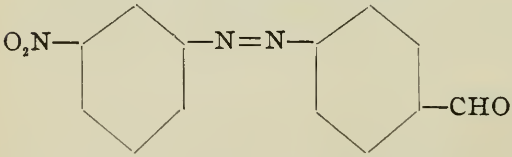
Nitroso compounds, under certain conditions, react almost quantitatively with amido compounds to produce azo compounds, according to the equation:

$$R.NO + H_2N.R' = R.N:N.R' + H_2O.$$

The most favorable conditions for this reaction seem to be those prevailing when a hot acetic acid solution of the nitroso compound is added to a boiling acetic acid solution of the amido compound. By slightly varying the conditions, it has been found, other reactions are induced. Thus, when a mixture of *p*-nitrosobenzaldehyde, *p*-toluidine, and glacial acetic acid is heated, a considerable quantity of *p*-azoxybenzaldehyde is formed.[1] We have found that *p*-nitrosobenzaldehyde condenses readily with *m*-nitraniline to produce the expected compound, *m*-nitrobenzene-*p*-azobenzaldehyde.

Ethyl *p*-nitrobenzoic ester, when treated with zinc and acetic acid, acts like the corresponding ethyl ester.[2] When the reduction-product is oxidized, ethyl *p*-azoxybenzoic ester is produced, together with ethyl *p*-nitrosobenzoic ester. The latter forms yellow crystals.

m-Nitrobenzene-p-azobenzaldehyde,



.—Two grams of *p*-nitrobenzaldehyde, dissolved in 25 cc. of glacial acetic acid, were slowly added to a boiling acetic acid solution of 4 grams of *m*-nitraniline. The mixture rapidly assumed a deep red color. It was kept hot for a few minutes and then allowed to cool slowly. Granular masses of crystals separated out. These were filtered out and washed on the filter with glacial acetic acid and with alcohol. The residue was transferred to a flask and covered with dilute nitric acid. After standing in contact with the nitric acid half an hour the solid was filtered out and washed with water. It was pure without further treatment.

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[1] Ber. d. chem. Ges., 36, 2310 (1903).

[2] *Ibid.*, 36, 2313 (1903).

	Calculated for $C_{13}H_9O_3N_3$.	Found.
N	16.5	16.8, 16.4, 16.4

m-Nitrobenzene-*p*-azobenzaldehyde forms granular masses, of indistinctly crystalline form and of orange-red color, melting at 223° (uncorr.). It is difficultly soluble in alcohol and in acetic acid.

Ethyl p-Nitrosobenzoic Ester, $ON.C_6H_4.CO.OC_2H_5$.—A solution of 5 grams of ethyl *p*-nitrobenzoic ester in 50 cc. of alcohol was treated with 10 cc. of glacial acetic acid and then with 4.5 grams of zinc dust. The last was added in small portions, the temperature of the mixture not being allowed to rise above 50°. The solution became brown, and on standing yellow crystals separated out. It was added to a mixture of 50 cc. of saturated potassium dichromate solution and 50 cc. of dilute sulphuric acid, a yellow precipitate being formed at once. The oxidation-product was distilled with steam. A green liquid collected in the receiver while a dark-colored, oily substance remained in the distilling-flask. Yellow crystals separated from the green distillate. These were twice recrystallized from alcohol.

	Calculated for $C_9H_9O_3N$.	Found.
N	7.8	7.7

Ethyl *p*-nitrosobenzoic ester forms yellow needles melting at 81° (uncorr.) to a green liquid. It forms green solutions.

Ethyl p-Azoxybenzoic Ester, $ON_2.(C_6H_4.CO.OC_2H_5)_2$.—The oily substance that remained in the distilling-flask in the preparation of the preceding compound solidified on cooling.

It was recrystallized from alcohol with the addition of charcoal. After the seventh recrystallization it consisted of orange leaflets, which melted to a turbid liquid at 113° (uncorr.). The latter became clear at 120° (uncorr.). This agrees with the observations of Meyer and Dahlem,[1] who obtained the same compound by the action of ethyl iodide upon the silver salt of *p*-azoxybenzoic acid. They obtained it in the form of yellow crystals. The orange color is probably due to traces of the red azo ester.

	Calculated for $C_{18}H_{18}O_5N_2$.	Found.
N	8.1	7.9, 8.0

UNIVERSITY PLACE, NEBRASKA,
June 15, 1904.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

X.—THE MOLECULAR WEIGHTS OF THE YELLOW NITROSO COMPOUNDS.

BY FREDERICK J. ALWAY AND ROSS A. GORTNER.

The nitroso compounds in which the nitroso group is attached to a carbon atom may be divided into three classes, according to the condition in which they exist in the solid form, *viz.*, (1) green or blue, (2) colorless or white, (3) yellow. It has been shown by Piloty,[2] Bamberger,[3] and Brühl[4] that the blue or green color depends upon the monomolecular condition, while the white or colorless form is evidence of the dimolecular condition. In an article by Alway and Bonner[5] it was shown that the only yellow nitroso compound known at that time, *p*-nitrosobenzaldehyde, possessed a normal molecular weight in solution in freezing acetic acid, in freezing benzene, and in boiling benzene. Since that time the methyl and ethyl esters of *p*-nitrosobenzoic acid[6] and of *p*-nitrosocinnamic acid,[7] as well as the acids themselves, have been obtained. All of these are yellow. We have determined the molecular weights of the four esters in freezing benzene. The acids, on account of the readiness with which they change into an insoluble form, are not well adapted to such determinations. The quantities of the *p*-nitrosocinnamic esters available for use were so small that the results in the case of these cannot be considered conclusive.

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[1] Ann. Chem. (Liebig), **326**, 337 (1903).
[2] Ber. d. chem. Ges., **35**, 3090, 3093, 3101 (1902).
[3] *Ibid.*, **33**, 3877 (1901).
[4] *Ibid.*, **31**, 1465 (1898).
[5] This JOURNAL, **30**, 111 (1903).
[6] Ber. d. chem. Ges., **36**, 2313 (1903).
[7] This JOURNAL, **32**, 394 (1904).

The *p*-nitrosobenzoic esters showed the normal molecular weight. The one *p*-nitrosocinnamic ester, which formed a greenish-yellow solution, gave a depression of the freezing-point corresponding to 50 per cent in the monomolecular form and 50 per cent in the dimolecular condition. The other *p*-nitrosocinnamic ester, which formed a yellow solution, gave a depression corresponding to the dimolecular condition.

Ethyl *m*-nitrosobenzoic ester, which we prepared for comparison with the corresponding methyl ester,[1] and which forms colorless crystals, exists in solution chiefly in the monomolecular condition. A small amount was present in the dimolecular condition at the temperature of freezing benzene.

In Experiments 1, 2, 3, 4, 5, and 6 the solutions were green and the color was not affected by changes of temperature. In Experiments 7 and 8 the solutions were green, but as the temperature fell the color diminished in intensity; on warming, the original intensity was restored. In Experiment 10 the solution was yellowish-green in color and no change was observed on lowering the temperature. In Experiment 9 the solution was yellow, without a distinctly green shade.

All the benzene solutions of the *m*- and *p*-nitrosobenzoic esters had changed to a red color after having stood several weeks in a dimly lighted room.

Ethyl m-Nitrosobenzoic Ester, $ON.C_6H_4.CO.OC_2H_5$.—Five grams of ethyl *m*-nitrobenzoic ester, dissolved in 50 cc. of alcohol, were treated with 10 cc. of glacial acetic acid and then with 5 grams of zinc dust, the latter being added in small portions and the mixture being kept well agitated. The yellow solution thus obtained was treated with ferric chloride solution and distilled with steam. A green liquid

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[1] Ber. d. chem. Ges., **36**, 2313 (1903).

Experiment No.	Dissolved substance.	Weight of solvent in grams.	Weight of dissolved substance in grams.	P'rc'nt'ge str'ngth of solution.	Depression of freezing-point.	Theoretical m'lecular weight.	Molecular weight found.
1	Methyl *p*-nitrosobenzoic ester	21.3980	0.1414	0.66	0°.215	165	153.0
2	“ “ “	“	0.2737	1.28	0°.430	“	149.0
3	“ “ “	“	0.3681	1.72	0°.555	“	155.0
4	Ethyl “ “	21.0980	0.2134	1.01	0°.290	179	174.0
5	“ “ “	“	0.3014	1.43	0°.400	“	179.0
6	“ “ “	“	0.3798	1.80	0°.480	“	187.0
7	“ *m*-nitrosobenzoic “	21.0526	0.1238	0.59	0°.145	“	199.0
8	“ “ “	“	0.2344	1.29	0°.285	“	227.0
9	Methyl *p*-nitrosocinnamic ester	21.7854	0.0772	0.35	0°.035	191	490.0
10	Ethyl “ “	21.3498	0.0956	0.45	0°.075	205	300.0

collected in the receiver. This, on standing, deposited white crystals, which were recrystallized from aqueous alcohol.

	Calculated for $C_9H_9O_3N$.	Found.
N	7.8	7.8

Ethyl *m*-nitrosobenzoic ester forms stellate groups of white crystals, which melt at 52° to 53° to a green liquid.

A brown substance, probably the azoxy ester, remained in the distilling-flask.

UNIVERSITY PLACE, NEBRASKA,
June 17, 1904.

REVIEWS.

THE OCCURRENCE OF ALUMINIUM IN VEGETABLE PRODUCTS, ANIMAL PRODUCTS, AND NATURAL WATERS. A Contribution to the Bibliography of the Subject. By C. F. LANGWORTHY, PH.D., and PETER T. AUSTEN, PH.D. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904.

"The material included in this contribution to the bibliography of aluminium deals only with the occurrence of this element in vegetable products, animal products, natural waters, and a few miscellaneous materials, such as edible earths. The general purpose has been to include only reference to such articles as report separate determinations of aluminium or some of its salts, and to omit the very large number in which iron and aluminium are reported together. In a few cases analyses have been cited which report 'traces' of aluminium, but the bulk of this material also has been omitted." In the four chapters, each of which is devoted to the occurrence of this element in one of the general sources stated above, the names of the authors are arranged alphabetically. The brief abstracts, averaging from three to eight lines, give the literature references and the percentage of aluminium found in the different cases. There is no discussion of the results, but where it has been deemed advisable, parts of the original articles are quoted. There are also several tables showing the percentage of aluminium phosphate in flour and in bread, aluminium in grape-juice, in tobacco and many other plant products, in waters, etc. The use of the book is made more convenient by means of an excellent index of 36 pages. It would be well to have a competent botanist correct the scientific names of the plants when the next edition is issued. Perhaps the authors of the articles are responsible for the mistakes noticed.

C. E. W.

A METHOD FOR THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions, Vol. I., containing classified descriptions of about 2,300 of the more important compounds of carbon with hydrogen and with hydrogen and oxygen. By SAMUEL PARSONS MULLIKEN, PH.D., Instructor in Organic Chemistry and Organic Analysis at the Massachusetts Institute of Technology, Boston, Mass. Large 8vo. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. xii + 264. Price, cloth $5.00.

In this book the author attempts to substitute a new method for the identification of pure organic compounds, based on physical properties and chemical reactions, for the one now generally used which he designates as the method of the empirical formula. At the present time the procedure is to analyze a substance and thus determine its percentage composition. The molecular weight is then determined or conjectured, and from these data the empirical formula is calculated. The properties of the substance are then compared with those of all the known compounds having this formula, and its identity is established. The new method proposes to make use of the more easily determined properties like qualitative elementary composition, color, melting-point, boiling-point, solubility, specific gravity, etc., for the purposes of identification. It rests upon a classification similar to that employed in botany. The compounds, or chemical "species," have been first grouped into "orders" on the basis of their qualitative elementary composition; then into "genera" (aldehydes, acids, phenols, etc.) usually on the basis of behavior in simple chemical tests; and finally, arranged within each genus according to the increasing value of some readily determined constant like the melting-point or boiling-point. The name of each species is followed in the tables by a brief specific characterization, enumerating some of the simpler properties of the substance that have genuine analytical significance, and then, whenever possible, by detailed directions for preliminary and corroborative tests which can be performed with small quantities of material.

The present volume takes up only the compounds of carbon with hydrogen and with hydrogen and oxygen, and, hence, the method is limited to comparatively few compounds. It is the intention of the author to extend the method to compounds containing nitrogen in a subsequent volume.

It is not to be denied that the method of combustion analysis is tedious and troublesome and requires a certain amount of skill on the part of the student using it and that chemists would hail a better method for the identification of organic compounds with delight. It seems to the reviewer, however, very questionable whether this new method is better than the old way. Even after locating an organic compound by means of its physical properties and chemical reactions, according to the new method, would not a careful chemist prefer to make a combustion analysis of the substance in order to be sure that he was right? The writer of this review remembers that some time ago he obtained a substance which had the properties of phenol and gave the chemical reactions of that substance, but it did not have the characteristic odor, and he was not sure that the substance was phenol until an analysis and a molecular weight determination showed that it had the composition represented by the formula C_6H_6O.

An enormous amount of work has been devoted to the book by the author, his pupils, and friends, and many of the tests have been worked out in detail so that they may be performed by any student with a little care.

The book is, singularly, free from errors, is well printed and bound, and is provided with a very excellent index. It will no doubt prove of value in identifying unknown organic compounds in the laboratory. W. R. O.

QUANTITATIVE ANALYSIS FOR MINING ENGINEERS. By EDMUND H. MILLER, PH.D., Adjunct Professor of Analytical Chemistry and Assaying in Columbia University. New York: D. Van Nostrand Company. 1904. pp. vii + 137.

This book consists of a series of articles on analytical chemistry which have been reprinted from the *School of Mines Quarterly*, and represents the work required of the mining engineers in Columbia University. It is not stated whether the book is supposed to present a systematic course on quantitative analysis, and from the material and its arrangement one is left in doubt in regard to this point. The first methods given are the usual elementary determinations of water, the SO_4, Mg, and Al ions in simple salts, but immediately following this is a chapter on the proximate analysis of coal. Then follow the gravimetric and volumetric methods for iron in ferric alum, and afterwards the determination of silica, phosphorus, and sulphur in iron ores.

From the first chapters one would suppose the book to be an elementary treatise; from the subsequent chapters an advanced work, especially so since the volumetric determination of iron is introduced without any discussion of volumetric principles. The book seems, therefore, to be a discussion of methods rather than a guide.

The subsequent chapters give the various gravimetric and volumetric methods for the analysis of iron and steel, the analysis of limestone, zinc in its ores, copper in ores and mattes, lead, antimony, and arsenic in ores, and the analysis of iron, manganese, lead, and copper slags, with a brief chapter on flue-gas analysis. Most of the methods are given with considerable detail and accuracy, but one receives a strong impression that the work is very uneven, and that much of it has been written hurriedly. In some places, particularly in the determination of carbon in steel, the directions are very meager, and the student is referred to other books for details. The processes for the various ores and slags are much better given, but throughout the book there is a lack of consecutive and logical statement of methods. The discussion of precautions and conditions, and the explanation of reactions, is well done and up to date. References to original articles are frequently given, and there is also an appendix of references, although we are sorry to see references in a few cases to translations rather than the original articles. The book is introduced by chapters on ionization and mass action, but this discussion is almost too brief and fragmentary to be of much use.

The relative size of the reading and advertising matter which the publishers have seen fit to insert is strongly suggestive of the 10-cent magazine. H. F.

THE ELECTRIC FURNACE. By HENRI MOISSAN. Authorized translation by VICTOR LENHER, PH.D., University of Wisconsin. Easton, Pa.: The Chemical Publishing Co. 1904. pp. 305.

A review of the French original of this book appeared in this JOURNAL in 1897.[1] Considering the lapse of time, it may be well to again call attention to the value of the book.

In 1892 Moissan constructed his little laboratory electric furnace, in which the heat of the arc was utilized, while the object heated was kept out of contact with the arc, thus entirely avoiding the electrical action of the arc while employing its thermal action; and also avoiding contamination by the vapor of carbon. With sufficient electrical current a temperature of 3500° can be obtained in a few minutes.

Using this furnace, Moissan and his pupils have done an immense amount of systematic work; indeed, the amount of accurate work is astounding if we recall the many important discoveries made by Moissan during this period which do not involve the use of the furnace; we need only refer to the hydrides of sodium and potassium, to the preparation of pure calcium, to the remarkable series of investigations at low temperatures.

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[1] "Le Four Électrique," This JOURNAL, 19, 623.

Although the furnace is so simple that any one can make it, and although it and various modifications of it were quickly listed by dealers at low price, it is a curious fact that little accurate research work has been done with it outside of Moissan's laboratory. As a rule, an important new apparatus or a new reaction of general application is scarcely made public before it is seized on by a host of workers—for example, the "Grignard reaction." That Moissan has been practically allowed a monopoly of this research work gives the book reviewed its value. It is a broad but fair statement, that our knowledge of chemical action at high temperatures is mainly due to Henri Moissan, and is recorded in this volume, which is therefore unique ; it is not a luxury nor a substitute for some other book on the subject, it is a necessity. A chemist who has not read it or the original papers in the *Comptes rendus*, does not know the properties of many of the pure metals, or of the different modifications of elementary carbon, or of the numerous carbides, borides, and silicides.

Attention was called in the previous review to the literary polish of the original. This is lacking in the translation, which is rough and occasionally obscure, but is literal, and has the advantage of additional matter bringing the work up to this year. E. R.

CHEMIE DER EIWEISSKÖRPER. Von DR. OTTO COHNHEIM, a. o. Professor der Physiologie an der Universität Heidelberg. Zweite vollständig neu bearbeitete Auflage. Braunschweig : Friedrich Vieweg und Sohn. 1904. pp. 315.

The appearance of the second edition of this remarkably complete and accurate book will be welcomed by all those who are interested in this subject. The great advance that has been made in the subject of proteid chemistry is made very apparent by comparing the second edition of this book with the first. The fundamental work of Hopkins and Cole, and of Fischer and his pupils, is treated of in detail. The literature up to January, 1904, is given. All who are interested in the subject of proteid chemistry should have access to this book. A. S. L.

GRUNDLINIEN DER ANORGANISCHEN CHEMIE. VON WILHELM OSTWALD. Zweite, verbesserte Auflage. Leipzig : Verlag von Wilhelm Engelmann. 1904.

The first edition of this book was reviewed in this JOURNAL at the time of its appearance three years ago. No essential changes have been made in the work in the preparation of this new edition. The introductory paragraphs have been reconstructed and the fundamental conceptions developed more clearly and sharply. For the expression "normal weight," used in the first edition, the expression "molar weight" has been substituted in this. Is this not too much of a concession to the molecular hypothesis? Of the atomic hypothesis the author says: "Auch in diesem Buche soll von diesem allgemeinen Gebrauche nicht wesentlich abgewichen werden. Doch läge es sicher im Interesse der Wissenschaft, wenn in dieser Berichtung eine grössere Vorsicht beobachtet würde, und deshalb ist hier Wert darauf gelegt worden, die Ausdrucksformen der Atomhypothese so sparsam anzuwenden, als es der Sprachgebrauch nur gestattet."

Ostwald's book has undoubtedly been of great service in showing teachers of chemistry how their subject may be developed logically. In order that a reformer may be even partially successful, it seems necessary for him to be an extremist. Some of us may squirm as we read Ostwald, but no doubt we are helped unless we are past help. It is an advantage to have even a few of the scales removed from our eyes. We are all groping. It is to be hoped that we are moving in the direction of the light. I. R.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XII. BAND. DIE ELEKTROCHEMISCHE INDUSTRIE DEUTSCHLANDS. Von P. FERCHLAND, DR. PHIL. Mit 4 Figuren und Tabellen im Text. Halle a. S. Verlag von Wilhelm Knapp 1904.

In the present number of this carefully prepared series of monographs the author gives an account of the historical development of electrochemical industries in Germany. In the 64 pages of the monograph are short chapters on the more important substances that are now prepared by electrical methods. Among other things, the way in which the water supply of cities can be purified by means of ozone, is described. This seems of especial interest in view of the copper sulphate method, which has come so prominently before the public in the last few months. There is an index of "persons and firms." C. E. W.

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DETERMINATION OF THE RELATIVE VELOCITIES OF THE IONS OF SILVER NITRATE IN MIXTURES OF THE ALCOHOLS AND WATER AND ON THE CONDUCTIVITY OF SUCH MIXTURES.

BY HARRY C. JONES AND H. P. BASSETT.

HISTORICAL SKETCH.

Such a large amount of work has been done, especially in the last few years, on the migration velocities of ions, that brief, but complete references to the investigations in this field will be given.

It was early noted that when an electric current is passed through a solution of an electrolyte, changes in concentration are produced. Faraday[1] pointed out that when an electric current is passed through a solution of an electrolyte, using copper electrodes, the solution around the cathode becomes lighter blue, while that around the anode becomes darker blue in color. This same phenomenon was observed two years later by Gmelin,[1] and Pouillet[2] observed a similar phenomenon in a solution of a salt of gold. Smee[3] advocated the theory, put forward ten years before by Faraday, that the hydrogen from the decomposed water acted upon the copper sulphate just as another metal would do. Daniell and Miller[4] electrolyzed the sulphates of copper and zinc, and showed that the two ions in each case traveled with different velocities.

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[1] Pogg. Ann., **32**, 436 (1834).

This was the state of the problem when Hittorf[5] undertook his elaborate experiments and showed conclusively that these differences in concentration were due to the differences in the velocities of the cation and the anion. Hittorf devised several forms of apparatus which, however, are the same in principle. They consist of a vertical tube divided into compartments by porous diaphragms. These diaphragms are the objectionable feature in the apparatus of Hittorf. Hittorf studied a number of questions, such as the effect of strength of current, concentration of the solutions, and temperature on the migration velocities.

The next important contribution to our knowledge in this field was that of F. Kohlrausch,[6] in which he showed that a very important relation exists between the velocities of the ions and the conductivity of solutions. In dilute solutions, under a given electromotive force, each of the ions moves through the liquid with a fixed velocity, dependent on its own chemical nature, and independent of that of the other ion. This he termed the law of the independent migration velocity of the ions. Expressed in other words, the velocity with which any ion travels is a constant for a given solvent and a given potential gradient, and is independent of the nature of the other ion or ions with which it is present in the solution. Representing the maximum molecular conductivity by $\mu\infty$ the law of Kohlrausch is formulated thus, $\mu\infty = c + a$, where c and a are the relative velocities of cation and anion, respectively.

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[1] Pogg. Ann., **44**, 5 (1838).
[2] Compt. rend., **20**, 1544 (1845).
[3] Phil. Mag., **17**, 196 (1840).
[4] Phil. Trans., I. (1844) ; Pogg. Ann., **64**, 18 (1845).
[5] Pogg. Ann., **89**, 177 ; **98**, 1 ; **103**, 1 ; **106**, 337, 513.
[6] Wied. Ann., **26**, 1 and 145 (1879).

The law of Kohlrausch has been modified by Ostwald[1] for solutions that are not completely dissociated, as follows: Representing the percentage dissociation by α, we have

$$\mu_v = \alpha(c + a).$$

It is, then, obvious that the law of Kohlrausch can be used to determine the velocity of ions. We can determine μ_v or $\mu\infty$ directly by the conductivity method, and we can determine the ratio of the two velocities by the Hittorf method. We have, then, the two equations:

$$\mu\infty = \mathrm{C} + \mathrm{A}; \qquad (1)$$

$$\frac{c}{a} = \frac{\mathrm{C}}{\mathrm{A}}. \qquad (2)$$

C and A represent the relative velocities of cation and anion at infinite dilution, and $\frac{c}{a}$ is the relative velocities as determined directly by the Hittorf method of electrolysis.

The first direct measurement of the absolute velocity of ions was made by Lodge.[2] By observing the rate at which hydrogen ions decolorize a layer of gelatine reddened by phenolphthalein, he was able to determine the rate at which the hydrogen ions moved under a given potential gradient.

The objection has been raised to the method of Lodge that the gelatine may have exerted an influence on the velocity of the ions, and, further, that the fall in potential along the tube was not regular. The agreement between the values found by Lodge and calculated by Kohlrausch shows that these sources of error could not have been serious.

Loeb and Nernst[3] devised a method for measuring the relative velocities of ions that did away entirely with the use of diaphragms. Their apparatus, which consisted essentially of a Gay-Lussac burette, and their method are open to serious objections. There is no means of properly separating the

[1] Lehrb. allg. Chem., II., 672.

[2] Brit. Assoc. Report, 1886, p. 393; 1887, p. 387.

[3] Ztschr. phys. Chem., 2, 948 (1888).

solutions after electrolysis, for the purpose of analysis, and it is much better to measure the current directly.

The method of Kistiakowsky,[1] and also that of Bein,[2] are quite similar to that of Loeb and Nernst, and the same objections apply to the latter as to the former.

Whetham[3] measured the absolute velocities of certain ions, avoiding the use both of diaphragms and gelatine solutions. He measured the velocity of the moving boundary between two solutions containing a common ion, one of the solutions being colored.

Schrader[4] devised a form of apparatus for determining migration velocities, which was essentially a modification of that used by Kistiakowsky. His apparatus, however, was bent in such a form that he could draw the solution off from either electrode, directly, for analysis.

Certain objections apply to all the methods thus far discussed for determining the migration velocities of ions. The earlier investigators either separated the solutions around the electrodes by means of porous diaphragms, or relied upon the difference in specific gravity resulting from the electrolysis to secure a separation.

Some of the objections to the earlier methods were removed by a form of apparatus devised by Jones and Mather.[5] The new feature of this was that it provided a means of separating completely the two solutions around the electrodes after the electrolysis was ended. The apparatus consists essentially of two vertical limbs united by a U-tube. At the bottom of the U-tube is a stop-cock, of large bore so as not to offer too much resistance to the passage of the current. The electrodes were introduced through ground-glass stoppers inserted into the bottoms of the upright tubes. After the electrolysis was ended the stop-cock was turned, and thus the portions of the solution on the two sides of the apparatus were completely separated. Each side could then be carefully washed out and the solution analyzed.

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[1] Ztschr. phys. Chem., **6**, 97 (1890).
[2] Wied. Ann., **46**, 29 (1892).
[3] Phil. Trans., A, 337 (1893).
[4] Ztschr. Elektrochem., **3**, 498 (1896).
[5] This JOURNAL, **26**, 473 (1901).

Mather worked on solutions of silver nitrate in alcohol, and found, as others had done in aqueous solutions, that with rise in temperature the velocities of cation and anion tended to become equal.

Since the above investigation was carried out in this University a number of pieces of work have been done on migration velocities. Gordon[1] studied the effect of change in temperature, especially with cadmium salts.

Hopfgartner's[2] work was similar in character to that of Schrader.

Kummel's[3] method is similar to that employed by Lodge.

The most elaborate investigation in the field that we are now considering, since the time of Hittorf, is that of Bein.[4] He described in all five forms of apparatus with various means of separating the solution around the cathode from that around the anode. In one form he used essentially the method described by Loeb and Nernst; in another the solutions are separated by a column of mercury. In general, it may be said that the apparatus devised and used by Bein is very complex, and in some cases probably much more so than necessary.

The next work to be considered in this connection is that of O. Masson,[5] who devised and used a new form of apparatus for measuring absolute velocities. Two flasks, each provided with a lateral opening, are connected by a graduated horizontal tube containing a mixed solution of gelatine and the salt to be investigated. Both anode and cathode solutions must be distinctly colored, the colored ion being the cation in the anode solution and the anion in the cathode solution. Further, the colored ions must migrate at a slower rate than the corresponding ions of the salt in the tube. A suitable anode solution is copper sulphate with a copper anode. A suitable cathode solution is sodium chromate with a platinum cathode.

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[1] Ztschr. phys. Chem., **23**, 469 (1897).

[2] *Ibid.*, **25**, 115 (1898).

[3] Wied. Ann., **64**, 655 (1898).

[4] Ztschr. phys. Chem., **27**, 54 (1898); **28**, 439 (1899).

[5] *Ibid.*, **29**, 501 (1899); Phil. Trans., A, **192**, 331.

When the current passes, the progress of the cation in the colorless solution in gelatine is accompanied by an equal advance in the blue copper ions. The colorless anions in the gelatine are, similarly, followed by the yellow chromium ions. The contents of the tube thus become blue at one end, colorless in the middle, and yellow at the other end. The relative lengths of the blue and yellow parts give the relative velocities of the cation and anion.

The relative velocities of the ions thus obtained are compared with Kohlrausch's values, and a fair agreement was found to exist. The absolute velocities in gelatine are somewhat smaller than in aqueous solution.

About this time Kohlrausch published an investigation on the velocities of ions in dilute aqueous solutions at 18°, and up to a concentration of one-tenth normal. He showed that, for solutions of from one-twentieth to one-tenth normal, the conductivities of compounds composed of univalent ions, or of univalent ions in combination with bivalent ions, may be calculated from the ionic velocities. This does not hold for compounds composed of bivalent ions only, since, for such the velocities vary with increasing concentration.

Among the later investigations on this subject is that of Steele.[1] The method which he employed is in principle similar to that used by Masson. The aqueous solution is imprisoned between partitions of gelatine containing the indicator ion in solution. The method of Steele, however, differs from that of Masson in two respects. The measurements of the relative velocities are made in water and not in gelatine, and the employment of a colored ion is not necessary. All that is required is that a solution of the indicator containing about the same number of gram-molecules per liter as the solution of salt whose ionic velocities are to be measured, should differ from the latter in density and refractivity. The choice of indicators is thus very largely increased. The results obtained

[1] J. Chem. Soc., 79, 414 (1901).

by this method agree very well with those found by other good methods.

A form of apparatus which differs very appreciably from that used by any previous investigator was designed and used by A. A. Noyes.[1] It consists essentially of two U-tubes attached by rubber tubing. The two arms of each tube are of unequal lengths, and the electrodes are inserted into the longer arms. The electrodes are of platinum, and the acid and alkali formed around the electrodes are titrated from burettes passing through stoppers into the longer arms of the U-tubes. By means of this apparatus, Noyes was able to measure the relative velocities of the ions of such salts as potassium chloride, sodium chloride, etc.

Thus far no work had been done in very dilute solutions, and it was important that this condition, especially, should be investigated. Jahn[2] and his pupils used a form of apparatus resembling in some respects that employed by Noyes. It consisted of a vessel of the form of an Erlenmeyer flask, connected with a U-tube, which, in turn, was connected with a larger part of the apparatus, whose size could be varied according to the dilution of the solution to be used. With their apparatus they measured the relative velocities of a few acids and quite a number of salts. They studied the effect of dilution upon the relative velocities of the ions, and found in many cases that the relative velocities did not become constant until a dilution of between 200 and 300 liters was reached.

Up to this time there was still a sharp limit in the dilution at which measurements of relative velocities had been made. This applies also to the work of Jahn, Noyes, and Bein. Jahn could not obtain accurate results above a dilution of 150 liters, and this dilution is not sufficient to measure the velocities of the ions of many salts.

Steele and Denison[3] undertook to measure the velocities of ions at dilutions comparable with those at which accurate conductivity measurements could be made, and also to test whether, at such dilutions, the relative velocities would become constant. Salts of calcium were employed because satisfactory conductivity measurements had been made to a high dilution. At a dilution of 300 or 400 liters a large volume of the solution must be subjected to electrolysis in order that an appreciable quantity of the salt would be carried by the current. With this idea in mind, they devised a form of apparatus which admits of the electrolysis of a large volume of the solution. A W-shaped tube was connected with a reservoir to which fresh quantities of the solution could be added as that in the apparatus was drawn off. The solution on each side of the apparatus could be drawn off separately, the apparatus refilled, and the electrolysis allowed to proceed until several liters of solution had passed through the apparatus. They worked with a number of salts, including potassium chloride.

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[1] Ztschr. phys. Chem., **36**, 61 (1901).

[2] *Ibid.*, **37**, 673 (1901).

[3] J. Chem. Soc., **81**, 456 (1902).

The values which they found for potassium chloride agree with the best results obtained by other investigators, and confirm Kohlrausch's assumption as to the constancy of migration velocities of the ions of salts of this class with increasing dilution.

Steele[1] continued the above investigation, using such salts as barium chloride and magnesium sulphate. He concluded that the velocity is not independent of the concentration, and that the velocity of the cation varies with the salt that is used. He explained the change in velocity with the concentration as due to the formation of complex ions in solution. This would mean a motion of at least a part of the undissociated salt along with the ions.

Abegg and Gauss[2] studied the effect of the initial concentrations of the neighboring electrolytes, and recommended that the concentration of the indicator jelly should be at least equivalent to that in the solution of the electrolyte under investigation.

The effect of electrical endosmose on transport numbers was investigated by Denison.[3] His method was essentially that employed by Steele. In this investigation he studied also the effect of gelatine on the transference numbers. He found that so long as the gelatine was liquid, it exerted no influence on the transference numbers. In solid gelatine the velocity of the cation is diminished relative to that of the anion. A similar phenomenon is observed in very concentrated aqueous solutions, and it is highly probable that in both cases the specific frictional coefficient of the ions, as well as the formation of complex ions, play an important part.

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[1] Phil. Trans., A., 198 (1901).

[2] Ztschr. phys. Chem., 40, 737 (1902).

[3] *Ibid.*, 44, 575 (1903).

Denison considers it probable that the gelatine combines with certain salts, forming complex cations. He also points out that various proteids have the power of combining with acids and alkalies, forming salt-like compounds.

It is thus very probable that gelatine, or some product of its hydrolysis, combines with the substance dissolved in it. This would explain the above difference in the transport numbers in liquid and solid gelatine.

Very little work has been done even up to the present on migration velocities in any solvent other than water. A few determinations have already been referred to, but they are very few in number. Still less has been done on transference numbers in mixed solvents.

Carrara[1] carried out an investigation on the migration velocities of ions in solutions in methyl alcohol. He worked with quite a number of salts, using three different forms of apparatus: One contained a membrane, and was similar to one of the forms used by Hittorf; another was the apparatus of Loeb and Nernst, while the third he describes as a new form of apparatus. This last form is a very slight modification of that devised and used by Jones and Mather in this University seven years ago. No mention is made by Carrara of this fact, doubtless due to an oversight on his part.

He brings out an interesting point in connection with lithium chloride. His results indicate the existence of complex ions in a solution of this salt, which is a binary electrolyte.

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[1] Gazz. chim. ital., **33**, I., 241 (1903).

On comparing the transport numbers found by Carrara in aqueous and methyl alcohol solutions, it is seen that the difference between them is very small, and of the same order of magnitude as the differences obtained by a change in concentration. In general, the transport number for the anion in methyl alcohol is higher than in water.

From these considerations he draws the conclusion that the transport numbers for the ions of an electrolyte tend towards the same value, independent of the solvent in which the electrolyte is dissolved. In other words, if the dilution is sufficiently great and no secondary reactions take place, the transport numbers of an electrolyte are the same in all solvents. The transport numbers found for solutions of salts in methyl alcohol are the same as in aqueous solutions at greater concentrations.

The most recent investigations in the field of migration velocities are those of Huybrechts[1] and of Wolff.[2] They used a form of apparatus which was a slight modification of that formerly employed by Jahn and his pupils.

As has already been stated, in most of the investigations aqueous solutions have been dealt with, and comparatively little work has been done in solvents other than water. The only investigations that have been carried out in any other solvent were those of Lenz, Mather, and the recent work of Carrara.

EXPERIMENTAL PART.

This investigation was undertaken for the purpose of determining what effect mixtures of methyl alcohol and water would have on the relative velocities of the ions of such a salt as silver nitrate.

The work of Jones and Lindsay[3] on the conductivity of certain salts in water, methyl, ethyl, and propyl alcohols, and mixtures of these solvents suggested this work.

In their work, Jones and Lindsay found that the conductivities of such salts as potassium iodide, ammonium bromide, strontium iodide, etc., were less in mixtures of the solvents than in either of the solvents alone. Especially was this the case in mixtures of methyl alcohol and water. Considering these facts, the first thing to determine was whether silver nitrate would give similar conductivity results, and if so, whether there was any relation between this phenomenon and the relative velocities. The conductivities of silver nitrate in these solvents and varying mixtures of them were determined. The water, methyl and ethyl alcohol, were purified by the methods described by Jones and Lindsay. In each case a mother solution was made in the solvent in question, and the remaining solutions were obtained by successive dilutions with some of the solvent of the same composition. In this way an error was avoided which would result from the contraction when alcohol and water were mixed, and also prevent the accompanying heat effect. In some cases, as in very dilute solutions, where such small quantities of the mother solution were required, a second mother solution was made from the first, and the more dilute solutions made from it in the way described. The strength of these mother solutions was determined by titrating with a standard solution of ammonium sulphocyanate.

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[1] Dissertation, University of Berlin, 1902.

[2] *Ibid.*, 1903.

[1] This JOURNAL, **28**, 329 (1902).

Conductivity Apparatus Employed.

The apparatus described and used was similar to that employed by Jones and Lindsay. The cells differed from the ordinary Arrhenius cell, being provided with a ground-glass top to prevent evaporation of the more volatile solvents, and also protect the anhydrous alcoholic solutions from the moisture of the baths and air. The glass tubes carrying the electrodes were passed through thin rubber tubes in the cap. Sealing-wax was then run over the outside of the joint.

The zero-bath was prepared as follows: A large glass battery-jar was filled with finely crushed ice and distilled water. It was then placed in a water-bath and the space between filled with finely crushed ice and water. This proved very efficient, as it was possible to keep within 0°.05 of zero for hours. The bath at 25° was of the ordinary form, and was kept in constant motion by a stirrer driven by means of a hot-air engine. The thermometers used could be accurately read to 0°.02. The burettes and flasks were carefully calibrated.

Conductivity Measurements.

All the conductivity measurements were made at the two temperatures, 0° and 25°. In the following tables $v =$ number of liters of solution containing a gram-molecular weight of the salt; $\mu_v 0° =$ molecular conductivity at 0°; $\mu_v 25° =$ molecular conductivity at 25°:

Table I.—Molecular Conductivity of Silver Nitrate in Water.

v.	μ_v 0°.	μ_v 25°.
10	55.72	99.46
20	58.63	105.72
40	63.10	110.22
80	63.16	115.81
160	65.38	119.86
320	69.91	125.08
640	71.05	125.86
1280	70.59	125.35

Table II.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
9.71	7.11	....
19.43	8.90	14.26
38.86	11.35	16.96
77.73	13.10	20.11
155.47	15.13	23.87
310.95	17.04	26.46
621.89	19.43	30.62

Table III.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
10	25.96	35.77
20	32.63	44.67
40	39.71	53.42
80	45.28	62.95
160	51.09	70.36
320	56.71	80.17
640	61.42	88.22

Table IV.—Molecular Conductivity of Silver Nitrate in 25 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
38.86	25.95	59.70
77.73	26.65	62.75
155.47	26.45	63.82
310.95	28.72	64.87
621.89	28.84	68.28

Table V.—Molecular Conductivity of Silver Nitrate in 50 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
19.43	15.25	37.87
38.86	15.81	39.50
77.73	17.04	42.42
155.47	17.92	45.15
310.95	19.10	47.13
621.89	19.90	49.39
1243.78	20.79	52.80

Table VI.—Molecular Conductivity of Silver Nitrate in 75 Per Cent Ethyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
19.43	13.12	27.01
38.86	14.30	30.43
77.73	16.79	33.65
155.47	19.48	35.94
310.95	18.00	39.01
621.89	19.41	40.14

Table VII.—Molecular Conductivity of Silver Nitrate in 25 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
40	35.63	72.68
80	36.95	75.56
160	39.03	79.34
320	41.03	82.93
640	41.23	83.91

Table VIII.—Molecular Conductivity of Silver Nitrate in 50 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
20	27.27	53.33
40	28.63	56.80
80	29.93	59.75
160	31.47	63.22
320	32.29	65.85
640	34.67	68.67

Table IX.—Molecular Conductivity of Silver Nitrate in 75 Per Cent Methyl Alcohol and Water.

v.	μ_v 0°.	μ_v 25°.
20	27.98	48.20
40	30.03	52.33
80	32.81	57.17
160	35.22	61.31
320	35.71	63.23
640	40.27	69.42

Table X.—Temperature Coefficients of Conductivity of Silver Nitrate in Water (0° to 25°).

v.	Temperature coefficient.
10	1.75
20	1.88
40	1.88
80	2.10
160	2.14
320	2.21
640	2.20
1280	2.19

Table XI.—Temperature Coefficient of Conductivity of Silver Nitrate in Ethyl Alcohol (0° to 25°).

v.	Temperature coefficient.
19.43	0.214
38.86	0.224
77.73	0.280
155.47	0.350
310.95	0.377
621.89	0.488

Table XII.—Temperature Coefficient of Conductivity of Silver Nitrate in Methyl Alcohol (0° to 25°).

v.	Temperature coefficient.
10	0.392
20	0.482
40	0.548
80	0.707
160	0.771
320	0.938
640	1.702

Table XIII.—Temperature Coefficients of Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Water of Various Compositions.

	Temperature coefficients.		
v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.
19.43	....	0.905	0.556
38.86	1.35	0.962	0.645
77.73	1.44	1.015	0.674
155.47	1.49	1.089	0.658
310.95	1.45	1.121	0.840
621.89	1.58	1.180	0.829
1243.78	....	1.280	....

Table XIV.—Temperature Coefficients of Conductivity of Silver Nitrate in Mixtures of Methyl Alcohol and Water of Various Compositions.

	Temperature coefficients.		
v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.
20	....	1.04	0.810
40	1.48	1.13	0.892
80	1.54	1.19	0.974
160	1.61	1.27	1.024
320	1.68	1.34	1.100
640	1.71	1.36	1.166

In order to see the connection existing between the conductivities in each solvent, the following tables are given for comparison :

Table XV.—Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of It with Water at 25° C.

v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
19.43	....	37.87	27.01	14.26
38.86	59.70	39.50	30.43	16.96
77.73	62.75	42.42	33.65	20.11
155.47	63.82	45.15	35.94	23.87
310.95	64.87	47.13	39.01	26.46
621.89	68.28	49.39	40.14	30.62

It is seen from these values that the molecular conductivity in ethyl alcohol and mixtures with water does not show a minimum in the ordinary range of dilution, but still does not obey the law of mixtures. This is in accordance with Jones and Lindsay's work on potassium iodide. In that case they did not find a trace of a minimum at 25°.

The values in Table XV. are plotted as curves in Fig. I.,

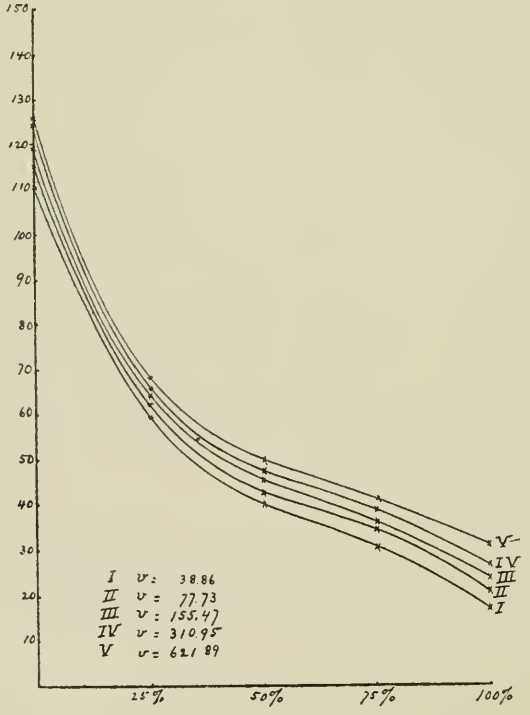

Fig. I.

the abscissae representing the different per cents of alcohol, and the ordinates the molecular conductivities.

Table XVI.—Comparison of the Molecular Conductivities of Silver Nitrate in Ethyl Alcohol and Mixtures of It with Water at 0° C.

v.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
9.71	....	....	....	7.11
19.43	....	15.25	13.12	8.90
38.86	25.95	15.81	14.30	11.35
77.73	26.65	17.04	16.79	13.10
155.47	26.45	17.92	19.48	15.13
310.95	28.72	19.10	18.00	17.04
621.89	28.84	19.90	19.41	19.43
1243.78	....	20.79	....	....

These values are plotted in Fig. II. The curves are of the same general form as in Fig. I. No distinct minimum is shown, but the form of the curve indicates that a minimum value is approached.

Table XVII.—Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of These Solvents at 25° C.

v.	Water.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
10	99.46	....	....	....	35.77
20	105.72	....	53.33	48.20	44.67
40	110.22	72.68	56.80	52.33	53.42
80	115.81	75.56	59.75	57.17	62.95
160	119.86	79.34	63.22	61.31	70.36
320	125.08	82.93	65.85	63.23	80.17
640	125.86	83.91	68.67	69.42	88.22
1280	125.35	....	....	....	....

These values are plotted in Fig. III. In nearly every case the minimum, as shown by the curve, lies between mixtures of the solvents containing respectively 50 and 75 per cent of alcohol.

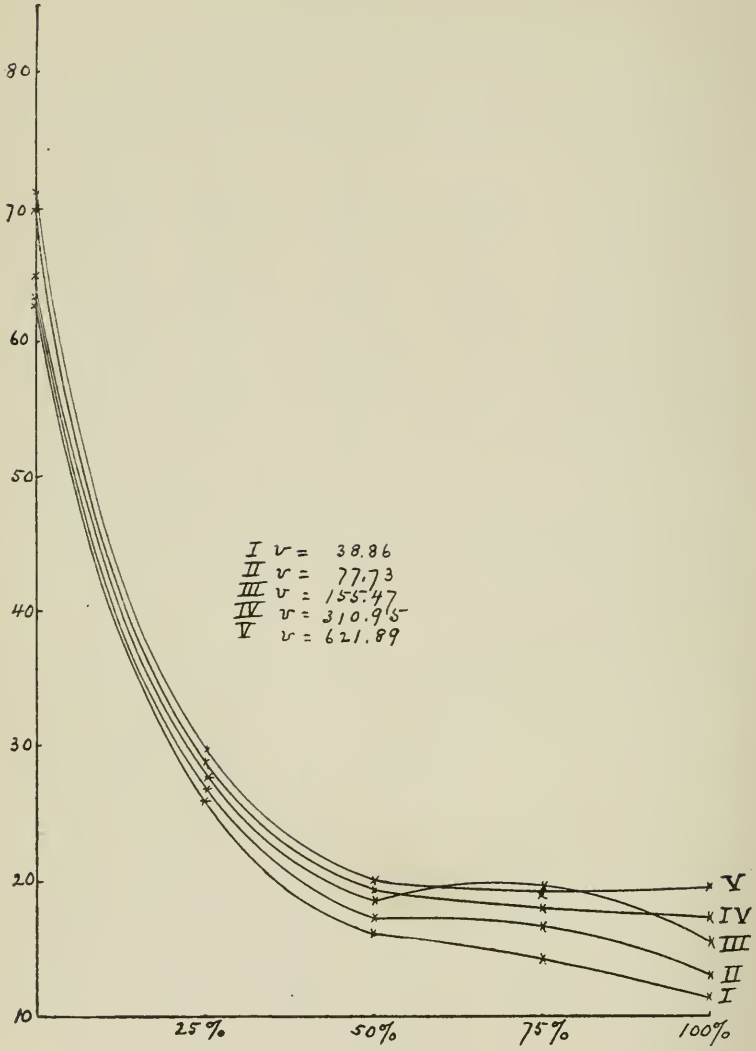
80
70
60
50
40
30
20
10
25%
50%
75%
100%
I v = 38.86
II v = 77.73
III v = 155.47
IV v = 310.95
V v = 621.89
V
IV
III
II
I

Fig. II.

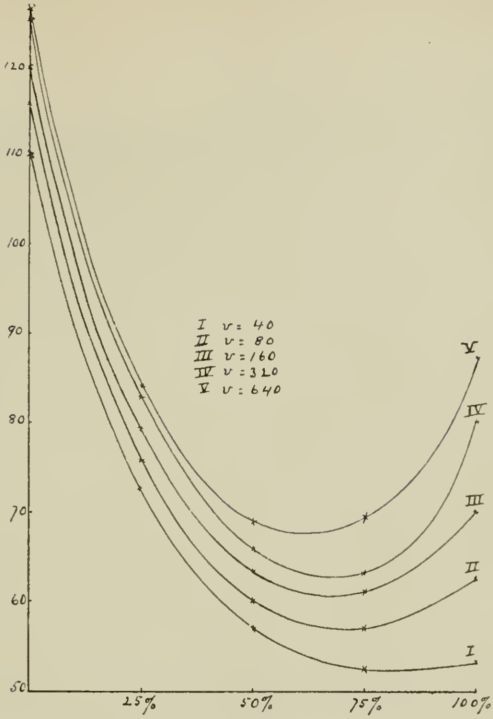

Fig. III.

Table XVIII.—Comparison of the Molecular Conductivities of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of These Solvents at 0° C.

v.	Water.	Twenty-five per cent alcohol.	Fifty per cent alcohol.	Seventy-five per cent alcohol.	One hundred per cent alcohol.
10	55.72	....	....	....	25.96
20	58.63	....	27.27	27.98	32.63
40	63.10	35.63	28.63	30.03	39.71
80	63.16	36.95	29.93	32.81	45.28
160	65.38	39.03	31.47	35.22	51.09
320	69.91	41.03	32.29	35.71	56.71
640	71.05	41.23	34.67	40.27	61.42
1280	70.59	....	....	....	....

These results are plotted in Fig. IV. The curves are of

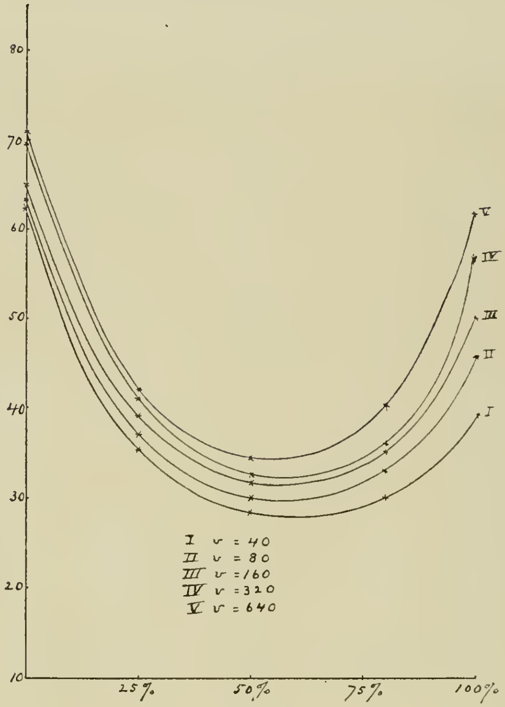

Fig. IV.

the same general form as the curves in Fig. III. They differ, however, in some respects. The chief difference is that the minimum point has shifted to the left, corresponding now to an alcohol-water mixture not far from 50 per cent.

From the above results it is clear that silver nitrate is not an exception to the general relation found by Jones and Lindsay. It was now interesting to see what effect alcohol would have upon the relative velocities of the ions, especially in the mixtures of methyl alcohol and water. This case seemed to offer a good field for investigation. Therefore, this particular part of the problem was taken up, and a few determinations of relative velocities were made in ethyl alcohol.

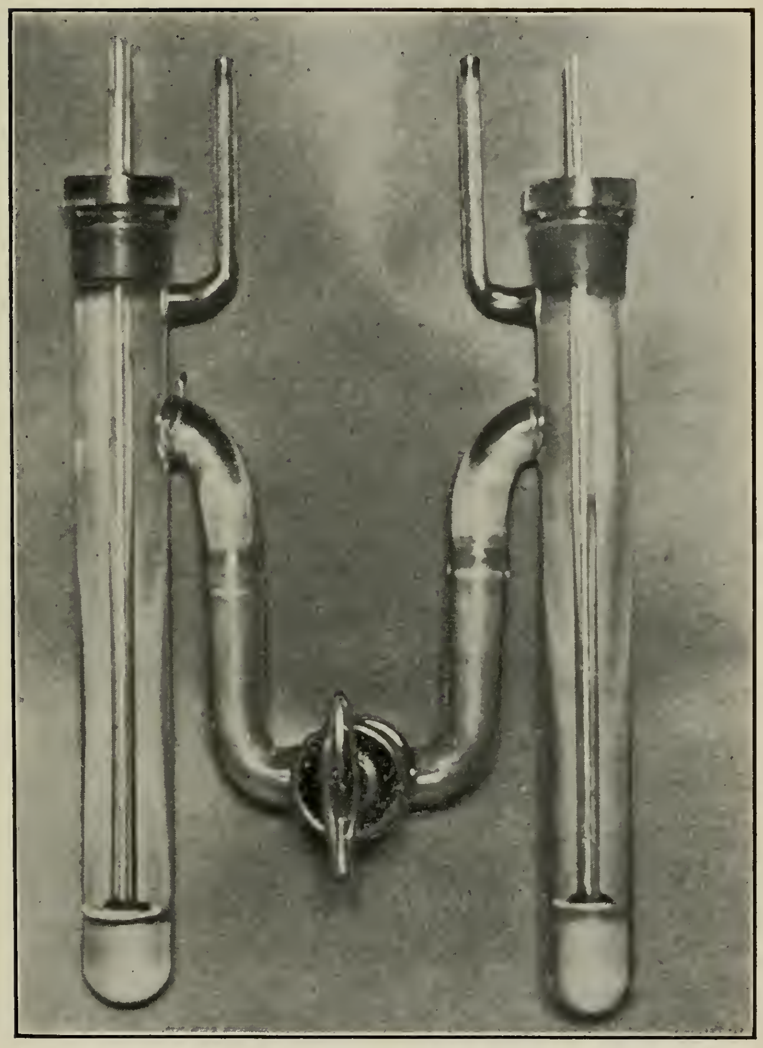

Plate I.

Relative Velocities of Ions.

In the last few years a large number of investigations have appeared on the relative velocities of ions. Most of them, however, have had to deal with aqueous solutions of a large number of substances. Few have determined the relative velocities in methyl and ethyl alcohol, and practically nothing has been done upon mixtures of these solvents.

In most of the later investigations new forms of apparatus have been devised, many of them being very complicated. The question arises whether such a high degree of complexity is necessary for effecting the electrolysis and separation of the solutions. In many of the new forms no special means were provided for the final separation of the solutions, some depending simply upon the difference in specific gravities of the solutions resulting from the electrolysis. Discrepancies in the results are, therefore, probably due in part to the incomplete separation of the two portions of the solution. But one form has been described which prevents diffusion. This apparatus was devised by Jones and Mather, in this University, and has already been fully described.

From an examination of the different forms of apparatus, that used by Mather seemed best adapted for this investigation, but some very serious difficulties, pointed out in part by Mather in his paper, had to be overcome. These difficulties, however, were avoided by devising the apparatus shown in Plate I.

The two limbs are 20 cm. long and 2 cm. in diameter, with the electrodes inserted from the top through ground-glass stoppers. Just below the stoppers two small tubes are attached, which extend outward and upward, the vertical part being graduated in millimeters. The lower part of this small tube is 5 mm. in diameter, and the vertical part is about 3 mm.

The limbs are connected, 3 cm. below the stoppers, by a U-tube 1.5 cm. in diameter, in the same plane with the limbs. The bottom of the U-tube is 5 cm. above the lower ends of the limbs. At the center of the U-tube is a stop-cock of 8 mm.

bore. The electrodes were made of pure, round, silver plates, into which a platinum wire was riveted in order to seal them into glass tubes running through the ground-glass stoppers. The small amount of platinum exposed in the bottom of the silver plate was covered by a thin coating of fusion glass. The glass tubes were then firmly secured in the ground-glass stoppers by means of a piece of black rubber tubing, which was placed on the tube and through which it was forced. The electrical connection was then made by filling the tubes with mercury, which made connection with the silver plate by means of the platinum wire riveted into the plate, as was stated above.

This form of apparatus could easily be placed in a thermostat on hooks arranged for that purpose, which supported the apparatus under the U-tube.

In order to keep a constant temperature, the thermostat-bath represented in Plate II. was constructed. This proved to be very efficient, remaining constant to within 0°.1, and at the same time affording plenty of room for three pieces of apparatus and voltameters. It consists of a wooden box 2 feet long, 14 inches wide, and 10 inches deep, lined inside with heavy galvanized iron. The iron lining extends to within one-half an inch of the top of the wooden box. One and one-half inches from the top of the box a heavy, movable shelf was arranged in which the three voltameters could be placed and kept at a constant temperature. In the bottom of the wooden box a hole 14 inches square was lined only with metal, so that a small flame could be applied. Hooks were arranged on the side of the bath opposite the shelf for the voltameters, and for the apparatus represented in Plate I., which was suspended from them. The bath was then filled with water to the level of the shelf and kept at constant temperature by means of an Ostwald thermoregulator. In order to secure a uniform temperature the water in the bath was kept in constant motion by a stirrer, which was driven by a small hot-air engine. For determinations at 0° the bath was filled with finely broken ice, and the apparatus placed in the bath in the same manner as in the 25° bath. The wooden casing of the bath,

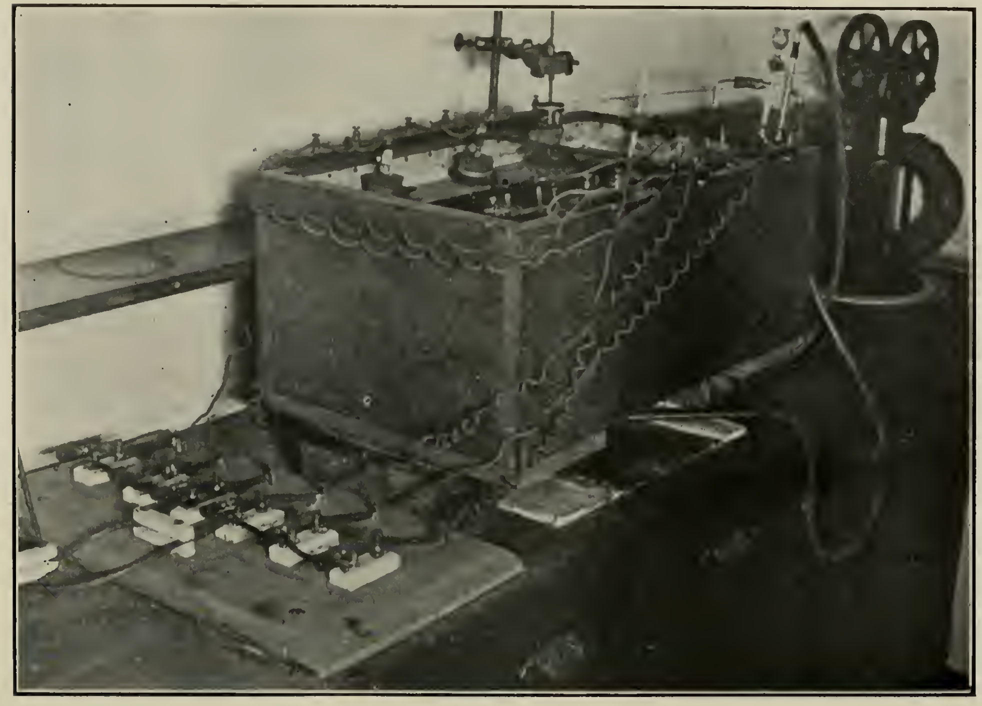

Plate II.

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in determinations at this temperature, serves as a poor conductor of heat. All of the electrical connections attached to the bath were placed upon a block of hard rubber to prevent any leak of current.

Special precautions were also taken in all the wiring about the bath. Flexible insulated wire was used, and wherever two wires crossed additional precaution was taken to run them through rubber tubing. The box was also covered thickly with shellac as an additional precaution. Two currents of different strengths were used. One current of 60 volts was supplied by a storage battery. The other current of 110 volts was supplied directly from the power house. In every case the current was measured by means of a voltameter, consisting of platinum crucibles and pure silver anodes. The platinum crucibles were placed in weighing-flasks to insulate them entirely from each other, and, at the same time, to serve as a convenient means of placing them upon their supports in the constant-temperature bath. Connections with the circuit were made by placing the platinum crucible upon a copper plate to which a wire had been soldered.

The anode of pure silver was suspended in the platinum crucible by running it through a rubber stopper, which fitted the weighing-glass and also served as a cover to it. The silver anode was also inserted into a clean linen bag to prevent any small particles, which become detached from the anode, from falling into the crucible and therefore being weighed with the silver deposited by the current.

The platinum crucibles were treated with fused acid potassium sulphate, then boiled with nitric acid, heated in the flame of the blast-lamp, cooled in a desiccator, and weighed before each experiment. The deposit formed by the current was treated in accordance with the directions recommended by Richards[1] in his investigation upon the determination of the chemical equivalent of copper and silver.

Preparation of Solutions.

The analysis in every case was made by titration with ammonium sulphocyanate, ferric ammonium sulphate being used as the indicator. Special care was taken in the preparation of the solutions, and their strength was determined by titration with standard solutions of potassium chloride.

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[1] Ztschr. phys. Chem., 41, 302 (1902).

In the preparation of the solutions of potassium chloride the pure salt, which had been purified especially for conductivity work, was used. Small amounts of this salt were weighed and dissolved in water. It was then titrated against the silver nitrate. The silver nitrate used was Kahlbaum's best material, which was free from any detectable impurities.

The water employed in the preparation of the solutions was obtained by redistillation of ordinary distilled water, essentially by the method described by Jones and Mackay.[1] The ordinary distilled water, to which a solution of chromic acid had been added, was boiled, and the steam passed through a boiling solution of barium hydroxide.

The absolute alcohol was prepared by distillation from quicklime, further dehydrated with anhydrous copper sulphate, and finally distilled from a small amount of sodium just before using. In the preparation of the solutions in absolute alcohol the following method was adopted: The silver nitrate was placed in a dry measuring-flask. The latter was filled with alcohol, by means of a siphon, from the bottle containing the alcohol which had been distilled from sodium. The alcohol was thus not allowed to come in contact with moisture. The bottle was closed by a two-hole rubber stopper. Through one hole the siphon passed, and through the other the drying-tube which permitted the air to enter the flask. The siphon led to a Gooch funnel, which was also closed with a two-hole rubber stopper; the siphon passed through one hole and another drying-tube through the other one. The funnel was connected with the measuring-flask and alcohol siphoned into it. The resulting solution of silver nitrate was then removed to a dry bottle which was closed with a rubber stopper, connection with the interior being made by a glass tube and drying-tube.

When it was desired to draw off part of the solution either for analysis or to fill the apparatus, the point of a burette was connected with the glass tube in the bottle by means of a rubber tube, and the solution was drawn up into the burette by aspiration through a drying-tube which closed its upper end. The burette was then connected with one of the small graduated tubes on the apparatus, the other one being closed by a Bunsen valve. The two small tubes were connected and the apparatus tilted first one way and then the other in order to remove the last trace of air from beneath the stoppers. Each tube was then closed with a Bunsen valve, and the apparatus placed in the constant-temperature bath. The connections with the circuit and voltameter being made, the electrolysis was begun.

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[1] This JOURNAL, 19, 91 (1897).

Calibration of Apparatus.

The first calibration of the apparatus was by weighing first the empty apparatus, then, with one side full of water, and finally with both sides full. In this way the exact contents of the apparatus could not be determined, but the ratio between the two sides could be obtained.

The second and subsequent calibrations were made by measuring the contents of each side with a burette, which had previously been calibrated by means of the apparatus designed by Morse and Blalock.[1]

Calibration No. 1, December 7, 1903.

Apparatus No. 1 :	
Weight of empty apparatus	287.95
" " apparatus with left side full of water	356.325
Weight of apparatus full of water	423.675
Therefore, right side contains	49.623 per cent
" left side contains	50.377 "
Apparatus No. 2 :	
Weight of epmty apparatus	265.52
" " apparatus with left side full of water	330.91
Weight of apparatus full of water	396.50
Right side contains	49.924 per cent
Left " "	50.076 "

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[1] This Journal, 16, 479 (1894).

Apparatus No. 3:

Weight of empty apparatus	267.79
" " apparatus with left side full of water	329.95
Weight of apparatus full of water	390.77
Right side contains	49.455 per cent
Left " "	50.545 "

Calibration No. 2, January 11, 1904.

Apparatus No. 1:

Contents of right side	67.71 cc.
" " left "	68.73 "
Right side contains	49.616 per cent
Left " "	50.384 "

Apparatus No. 2:

Contents of right side	65.39 cc.
" " left "	65.21 "
Right side contains	50.07 per cent
Left " "	49.93 "

Apparatus No. 3:

Contents of right side	62.44 cc.
" " left "	63.34 "
Right side contains	49.485 per cent
Left " "	50.515 "

Calibration No. 3, February 15, 1904.

Apparatus No. 1:

Contents of right side	68.43 cc.
" " left "	68.61 "
Right side contains	49.934 per cent
Left " "	50.066 "

The position of electrodes in this apparatus was changed just before the calibration.

Apparatus No. 2:

Contents of right side	65.82 cc.
" " left "	65.42 "
Right side contains	50.114 per cent
Left " "	49.886 "

Apparatus No. 3:

Contents of right side	62.30 cc.
" " left "	63.64 "
Right side contains	49.468 per cent
Left " "	50.532 "

Calibration No. 4, March 21, 1904.

Apparatus No. 1 :	
Contents of right side	68.56 cc.
" " left "	68.66 "
Right side contains	49.963 per cent
Left " "	50.037 "
Apparatus No. 2 :	
Contents of right side	66.10 cc.
" " left "	65.85 "
Right side contains	49.447 per cent
Left " "	50.533 "
Apparatus No. 3 :	
Contents of right side	62.45 cc.
" " left "	63.85 "
Right side contains	49.447 per cent
Left " "	50.553 "

Measurement of Relative Velocities.

Knowing the relation between the two sides of the apparatus, the experiments were carried out as follows : The apparatus was filled from the burette, as described above, to the zero mark on each side. The open ends of the small leveling limbs were then closed by Bunsen valves, and the whole placed in the bath by supporting it on hooks arranged for that purpose. The water in the bath and the solution in the apparatus were practically the same height, as the apparatus was immersed until the bottom of the ground-glass stoppers were on a level with the surface of the water.

Connection with the circuit and voltameters being made, the electrolysis was allowed to proceed until enough silver was deposited in the voltameters to be weighed accurately, the deposit usually weighing between 0.05 to 0.10 gram. The time of the electrolysis depended upon the resistance offered by the solution. At the close of the electrolysis the apparatus was removed from the bath, and the level of the solution in the apparatus brought to corresponding graduations on each leveling-tube. The stop-cock was then closed and the contents were carefully washed, filtered through glass wool or washed asbestos to remove any disintegrated silver, made up to a known volume, and analyzed. The accuracy of the results was determined by comparing the amount of silver found on analysis with that calculated from the amount of solution placed in the apparatus at the beginning of the experiment. With this data the relative velocities of the ions could easily be calculated as follows: The amount of silver found in the apparatus as a whole was multiplied by the per cent contained on the side that increased, thus giving the amount of silver contained on that side at the beginning of the experiment. This was then subtracted from the amount found on that side by analysis, which gave the amount of increase due to electrolysis. This increase was then divided by the weight of the silver deposited in the voltameter, the result being the relative velocity of the anion. The strength of the current in no case exceeded 0.005 ampere.

Silver Nitrate in Water.

In these determinations the apparatus was filled, and the experiment carried out as described above. After the electrolysis each side was carefully washed out, filtered through glass wool, and diluted to 200 cc. Aliquot parts of this were then taken and titrated against a standard solution of ammonium sulphocyanate. At the beginning of this investigation the titrations of several of the determinations were made with N/10 ammonium sulphocyanate, but it was soon found that this was too concentrated to give good results, since the burette could not be read with sufficient accuracy to obviate a large experimental error. Another very serious difficulty was that in titrating such a strong solution against a comparatively weak one, in many instances, the smallest fraction of a drop that could be used would go considerably beyond the neutral point.

To prevent these experimental errors the titrations were made with a N/25 solution of ammonium sulphocyanate. With a solution of this strength the point of change could easily be distinguished, and the error in reading the burette would be diminished, since a larger volume of solution would be used. The results of these determinations are given in the following table. In this, as in all subsequent tables, the following symbols will be used:

t = temperature of the bath.

m = concentration of the solution in gram-molecular weights per liter.

c = change in concentration expressed in number of cubic centimeters of N/10 silver nitrate.

v = amount of silver in grams, deposited in the voltameter.

a = velocity of the anion.

Table XIX.—Relative Velocity of the Anion of Silver Nitrate in Water at 25°.

t.	*m.*	*c.*	*v.*	*a.*
25°	0.1	20.964	0.4320	0.5238
25°	0.1	20.034	0.4126	0.5260
25°	0.1	12.705	0.2622	0.5230
25°	0.1	12.452	0.2535	0.5301
25°	0.1	13.008	0.2587	0.5387

Values obtained by other observers, although at different temperatures, are given in the following table:

Table XX.—Relative Velocity of the Anion of Silver Nitrate Determined by Other Observers in Aqueous Solution at Different Temperatures.

t.	*m.*	*a.*	
29°.1	0.1	0.5317	Mather
45°	0.025	0.5246	"
47°.7	0.1	0.5280	"
47°.9	0.1	0.5272	"
47°.4	0.1	0.5286	"
19°	0.118	0.526	Hittorf
19°	0.055	0.526	"
19°	0.024	0.526	"
20°	0.1043	0.528	Nernst and Loeb
26°	0.0521	0.524	" " "
26°	0.0230	0.522	" " "
26°	0.0105	0.523	" " "

Table XXI.—Relative Velocity of the Anion of Silver Nitrate in Aqueous Solution at 0° C.

m.	*c.*	*v.*	*a.*
0.102	6.3370	0.1214	0.5633
0.102	6.4940	0.1229	0.5622
0.102	6.2480	0.1198	0.5629

Table XXII.—Relative Velocity of the Anion of Silver Nitrate as Determined by Other Observers in Aqueous Solution at 0°.

m.		
0.1	0.5414	Mather
0.1	0.5401	‘‘
0.1	0.5413	‘‘
0.025	0.5377	‘‘
0.025	0.5380	Nernst and Loeb

These values differ considerably from those obtained in this investigation at the same temperature. In the determination of the first three by Mather, he measured the current with a d'Arsonval galvanometer, and by this means only determined the average strength of the current, thus probably introducing a considerable experimental error.

In the last two determinations in Table XXII. the current in both cases was measured by a silver voltameter, but the concentration of the solution was less, and, as is well known, a decrease in concentration diminishes the relative velocity of the swifter ion.

Table XXIII.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25° C.

m.	*c.*	*v.*	*a.*
0.1012	2.893	0.0510	0.6122
0.0763	5.584	0.1021	0.5903
0.0763	5.580	0.1013	0.5945
0.0784	5.343	0.0942	0.6121
0.094	3.625	0.0663	0.5903
0.094	4.617	0.0840	0.5932

The solutions of silver nitrate in ethyl alcohol offered great resistance to the current, and where the large changes in concentration were obtained the current was allowed to run for ten or twelve hours.

Table XXIV.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25° C.

m.	*c.*	*v.*	*a.*
0.100	8.964	0.1655	0.5849
0.100	8.971	0.1684	0.5800
0.100	8.222	0.1517	0.5849
0.098	5.891	0.1098	0.5789
0.098	5.726	0.1086	0.5700

A much larger change in concentration was obtained in these determinations than in those in ethyl alcohol, because the silver nitrate was considerably more soluble in methyl than in ethyl alcohol, and thus the electrolysis could proceed further without danger of the determination being lost on account of the cathode and anode liquids becoming mixed.

Table XXV.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.

m.	*c.*	*v.*	*a.*
0.097	3.4570	0.0639	0.5823
0.097	3.8530	0.0722	0.5898
0.096	3.1447	0.0572	0.5933
0.096	2.2730	0.0422	0.5861
0.096	3.0962	0.0572	0.5842

Table XXVI.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 25 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.1	6.6280	0.1285	0.5567
0.1	6.4530	0.1258	0.5536
0.1	6.2880	0.1231	0.5513

Table XXVII.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.103	3.762	0.0748	0.5428
0.103	3.682	0.0741	0.5368
0.104	4.045	0.0821	0.5317
0.104	4.089	0.0822	0.5375
0.104	4.255	0.0851	0.5396
0.104	4.274	0.0854	0.5402
0.104	4.316	0.0851	0.5474
0.103	3.197	0.0654	0.5276

Table XXVIII.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.104	6.176	0.1104	0.6037
0.104	6.310	0.1128	0.6037
0.104	6.147	0.1114	0.5955

Table XXIX.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.1048	2.8080	0.5730	0.5289
0.1048	3.1540	0.6410	0.5308
0.1048	3.1140	0.6340	0.5301

Table XXX.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75 Per Cent Methyl Alcohol and Water at 25°.

m.	*c.*	*v.*	*a.*
0.104	6.058	0.1106	0.5912
0.104	4.534	0.0832	0.5881
0.104	4.474	0.0820	0.5888
0.107	1.903	0.0348	0.5902
0.107	2.954	0.0538	0.5926

Table XXXI.—Relative Velocity of the Anion of Silver Nitrate in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0°.

m.	*c.*	*v.*	*a.*
0.099	3.092	0.0589	0.5666
0.099	3.021	0.0578	0.5641
0.099	3.055	0.0580	0.5686
0.096	3.000	0.0571	0.5670
0.098	3.033	0.0575	0.5693
0.095	1.680	0.0319	0.5685

In order to see the connection existing between the relative velocities of the anion of silver nitrate in water, methyl alcohol, and the various mixtures of these solvents, the following table is given :

Table XXXII.—Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of these Solvents.

t.	0.	Twenty-five per cent.	Fifty per cent.	Seventy-five per cent.	One hundred per cent.
25°	0.5285	0.5538	0.6010	0.5902	0.5797
0°	0.5628	0.5379	0.5299	0.5673	0.5871

The values in this table are plotted in Fig. V., the abscissae representing the per cent of alcohol and the ordinates representing the relative velocity. The curve at 25°

shows a maximum value in the 50 per cent mixture, while at 0° a minimum value is shown in the same solvent. The curves are also exactly opposite in every respect. The course of the curves may be explained as follows: The law of Kohlrausch[1] shows that the molecular conductivity at infinite dilution is equal to the sum of two independent constants, which are in fact the velocities of the ions at infinite dilution calculated in terms of conductivity units, that is,

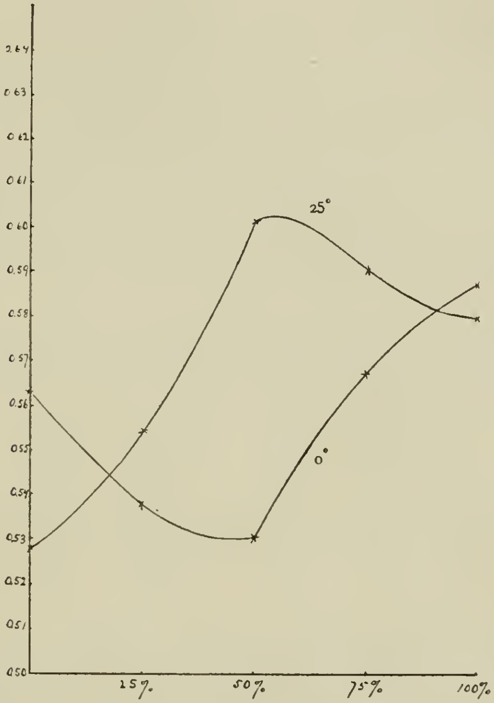

Fig. V.

$$A + C = \mu\infty,$$

A representing the anion, C the cation, and $\mu\infty$ conductivity at infinite dilution.

In this investigation, however, the conductivity at infinite dilution in these various solvents has not been determined, but by Ostwald's[1] modification of the law of Kohlrausch, which takes into account the amount of dissociation,

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[1] Wied. Ann., **26**, 194 (1895).

$$\alpha(A + C) = \mu\infty,$$

α representing the per cent of dissociation, it is possible to calculate αA and αC at any dilution if the ratio C/A is known. The ratio C/A has been determined for a N/10 solution of silver nitrate in these various solvents.

Hence, if we have the conductivities at 0° and at 25° of any dilution, we may calculate αC and αA, assuming that C/A is practically the same for dilutions of about the same order, which is not improbable. This has been done in the following table for a dilution of $v = 40$.

Table XXXIII.—Velocities of the Anion and Cation of Silver Nitrate in Water, Methyl Alcohol, and Mixtures of these Solvents Calculated in Conductivity Units.

	CH_3OH. 0 per cent.	CH_3OH. 25 per cent.	CH_3OH. 50 per cent.	CH_3OH. 75 per cent.	CH_3OH. 100 per cent.
Anion, 25°	58.25	40.24	34.65	30.88	30.96
" 0°	35.51	19.18	15.71	17.04	23.31
Cation, 25°	51.97	32.44	22.15	21.45	22.46
" 0°	27.59	16.46	12.92	12.99	16.40

Having calculated these values of C and A for the two temperatures, 0° and 25°, we may calculate the temperature coefficients of ionic mobility, not the true coefficients, however, but α (a constant) times the true coefficient. The variation of α, as was shown by Jones and Douglas,[2] is not appreciable over a range of 25°, and, therefore, the above procedure is allowable. This has been done in the following table.

A_{25} represents the ionic velocity of the anion at 25°, measured in conductivity units.

A_0 represents the ionic velocity of the anion at 0°, measured in conductivity units.

ΔA represents the difference in the velocities of the anion, between 0° and 25°, or is equal to $A_{25} - A_0$.

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[1] Lehrbuch d. allg. Chem., II., 672.

[2] This Journal, **26**, 428 (1901).

C_{25} represents the ionic velocity of the cation at 25°, measured in conductivity units.

C_0 represents the ionic velocity of the cation at 0°, measured in conductivity units.

C represents the difference in the velocities of the cation between 0° and 25°, or is equal to $C_{25} - C_0$.

φ_{25} represents fluidity of the solvent at 25°.

$\Delta\varphi$ represents the difference in the fluidity between 0° and 25°, or is equal to $\varphi_{25} - \varphi_0$.

Δt represents difference in temperature, or 25° — 0°.

φ_0 represents fluidity of the solvent at 0°.

Table XXXIV.—Comparison of the Relative Temperature Coefficients of Ionic Mobility for the Ions of Silver Nitrate in Water, Methyl Alcohol, and Various Mixtures of these Solvents, also the Temperature Coefficient of Mobility of Solvent.

	CH_3OH. 0 per cent.	CH_3OH. 25 per cent.	CH_3OH. 50 per cent.	CH_3OH. 75 per cent.	CH_3OH. 100 per cent.
$\frac{1}{A_{25}} \cdot \frac{\Delta A}{\Delta t}$	0.0156α	$0.0209\alpha_1$	$0.0230\alpha_2$	$0.0179\alpha_3$	$0.0098\alpha_4$
$\frac{1}{C_{25}} \cdot \frac{\Delta C}{\Delta t}$	0.0189α	$0.0197\alpha_1$	$0.0166\alpha_2$	$0.0153\alpha_3$	$0.0106\alpha_4$
$\frac{1}{\varphi} \cdot \frac{\Delta \varphi}{\Delta t}$	0.0249	0.0223	0.0216	0.0205	0.0121

The temperature coefficients of mobility of the solvents were calculated from the results of Traube,[1] Pagliani,[2] and Batelli.[3] The relative temperature coefficients for the anion and cation in the same solvent are strictly comparable, since α is a constant and therefore does not affect the result of the comparison.

From a consideration of these data it is seen that, in the pure solvents, water and methyl alcohol, the coefficient for the cation is greater, whereas in the mixture, that of the anion is greater. This being the case, C/A in the pure solvents would approach the limiting value 0.5, as the temperature rises, and the beginning and end of the curve of relative velocities at 25° would be below the beginning and end of the curve for 0°.

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[1] Ber. d. chem. Ges., 19, 871 (1889).

[2] Att. d. R. Ac. delle. Sc. d. Torrino.

[3] *Ibid.*

Since in the mixtures the anion has a larger temperature coefficient, the curve for 25° will pass through a maximum, this maximum existing in that mixture where the irregularity between the two temperature coefficients is greatest, that is, the 50 per cent mixture.

If we know the value of α, the dissociation factor, we could calculate the true temperature coefficients from the relative coefficients.

At the dilution used ($v = 40$) the dissociation of silver nitrate in water is about 89 per cent, or $a = 0.89$. It has been shown by Jones and Carroll[1] in the case of certain salts, sodium iodide, potassium iodide, and potassium bromide, that in 50 per cent methyl alcohol $a = 0.91$ for $v = 32$, and 0.93 for $v = 64$. We should not make an appreciable error if we assume the value 0.91 for a in the case of silver nitrate in the 50 per cent mixture at $v = 40$. The real temperature coefficient would then be $0.0230 \times 0.91 = 0.0212$. Kohlrausch[2] has pointed out in the case of certain ions in aqueous solutions that the more nearly the temperature coefficients of ionic mobility and fluidity (of water) are equal, the greater is the effect of decrease in fluidity in lowering ionic mobility. This would probably be true for ions in mixed solvents.

Comparing, then, the temperature coefficients of mobility of anion and cation, and fluidity of the 50 per cent mixture, it is seen that the temperature coefficient of the $\overline{NO_3}$ ion (0.0212) is most nearly equal to that of fluidity (0.0216). Hence the effect of decrease in fluidity would be greatest in the case of the $\overline{NO_3}$ ion; that is, C/A would approach the limiting value 0.5, and, hence, the minimum in the curve in the 50 per cent mixture.

The fluidity is also decreased by change of composition, and the resulting change in ionic mobility will be greatest in the case of that ion whose temperature coefficient is most nearly equal to the temperature coefficient of fluidity. This is the case with the $\overline{NO_3}$ ion; therefore, this ion will be the most affected, and the ratio between its velocity and that of the $\overset{+}{Ag}$ ion will become less, that is, approach the limit 0.5 and there will therefore be a minimum in the curve.

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[1] This JOURNAL, 32, 521 (1904).

[2] Sitz. Ber. d. Berlin Ak., 1902, p. 572.

Conclusions.

1. A study of the conductivity of silver nitrate in water, methyl alcohol, and mixtures of these solvents, leads to the conclusion that silver nitrate is not an exception to the general phenomenon discovered by Zelinsky and Krapiwin[1] and studied extensively by Jones and Lindsay in this University. The minimum point in the conductivity was found for silver nitrate in these solvents at 25° as well as at 0°.

2. The conductivity of silver nitrate in water, ethyl alcohol, and mixtures of these solvents does not show a minimum point either at 25° or at 0°, but a study of the curves representing these conductivities leads to the conclusion that at 0° a minimum is approached.

3. By comparing the conductivities at 0° with those at 25° the conclusion can be drawn that the influence of one solvent on the other decreases with rise in temperature.

4. The difference in the relative velocities observed in the pure solvents at 0° and 25° become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the case of mixed solvents. That exactly the opposite is true in most mixtures is seen by examining Fig. V.

5. The relative velocities are largely dependent on the nature of the solvent.

6. In mixed solvents the relative velocities are dependent on both the temperature and composition of the mixture.

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[1] Ztschr. phys. Chem., **21**, 35 (1897).

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE REACTIONS OF ETHYL CHLORSULPHONATE.

BY O. W. WILLCOX.

Ethyl chlorsulphonate, $C_2H_5OSO_2Cl$, was first prepared by R. Williamson,[1] in 1857, and has since been studied by a number of chemists. The latest of these investigations was carried out in this laboratory by Bushong,[2] who studied its behavior towards sodium alcoholates and aniline and proved that it acts as an alkylating agent.

At the suggestion and under the supervision of Dr. J. U. Nef I have undertaken a further study of this interesting compound, with special reference to a complete and final explanation of all the reactions shown by it.

As is clearly evident from the work of Nef,[3] the alkylating properties of primary and secondary esters of sulphuric acid are due to the fact that the organic radicals in these compounds undergo a methylene dissociation. Ethyl sulphuric acid, for example, is partially dissociated at ordinary temperatures into ethylidene and sulphuric acid,

$$CH_3CH_2OSO_2OH \rightleftarrows CH_3CH= + H{-}OSO_2OH.$$

The well-known alkylating properties of the alkyl haloids, alkyl nitrates, sodium alcoholates, $C_nH_{2n+1}X$, $C_nH_{2n+1}ONO_2$, $C_nH_{2n+1}ONa$, are similarly due to the presence of dissociated methylene residues, $C_nH_{2n}=$, and the speed of the alkylation in the different cases must therefore be directly proportional to the percentage of such residues present at the reaction temperature—a fact which has been qualitatively verified by Nef's work, and which has also, in part, been demonstrated quantitatively by various observers.[4]

Since the work of Bushong obviously shows that ethyl chlorsulphonate is an alkylating agent, a dissociation of this substance into ethylidene and chlorsulphonic acid,

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[1] J. Chem. Soc. (London), **10**, 97.

[2] This JOURNAL, **30**, 212.

[3] Ann. Chem. (Liebig), **309**, 126-189; **318**, 1-57.

[4] Conrad: Ztschr. phys. Chem., **3**, 450; **4**, 631. Menschutkin: *Ibid.*, **5**, 589; **6**, 41. Burke and Donnan: J. Chem. Soc. (London), **85**, 555.

$$CH_3CH_2OSO_2Cl \rightleftarrows CH_3CH= + H—OSO_2Cl,$$

must exist and be capable of experimental demonstration. Whereas ethyl chloride does not dissociate completely into ethylene and hydrochloric acid until 550°, the dissociation-point of ethyl chlorsulphonate was found to be very low—namely, at 160°. Consequently the latter substance is, like diethyl sulphate, a far more energetic alkylating agent than chloride, bromide, or even iodide of ethyl.[1] It reacts, for instance, with ammonia in absolute ethereal solution with violence at 0°, giving a mixture of di-, tri-, and tetraalkylated ammonium chlorides. Under similar conditions a reaction with ethyl chloride and ammonia is hardly perceptible, and even with ethyl iodide proceeds only very slowly.

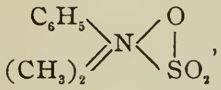
Incidentally, it was also demonstrated by experiment that chlorsulphonic acid—the other dissociation-product of ethyl chlorsulphonate—is partially dissociated further into sulphur trioxide and hydrogen chloride,

$$ClSO_2OH \rightleftarrows O_2S=O + H—Cl.$$

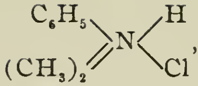
Since the products of dissociation of chlorsulphonic acid interact spontaneously on one another at 170°, or in the presence of catalytic agents even at 70°, with formation of equal molecules of sulphuryl chloride and sulphuric acid,[2]

$$2SO_3 + 2HCl \rightarrow SO_2Cl_2 + H_2SO_4,$$

it was impossible to determine the exact dissociating-point of chlorsulphonic acid, but it is undoubtedly low—not above 250°. Consequently, there must be a relatively large percentage of dissociated chlorsulphonic acid particles, SO_3 and HCl, present at ordinary temperatures in a preparation of chlorsulphonic acid. This was demonstrated in a most striking manner by treatment of this substance, in chloroform solution at 0°, with dimethylaniline, dimethylaniline sulphurtrioxide,



$\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}\!>N<\begin{matrix}O\\|\\SO_2\end{matrix}$

, and the hydrochloride of dimethylaniline,  $\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}\!>\!N\!<\!\begin{matrix}H\\Cl\end{matrix}$, being quantitatively formed.[1]

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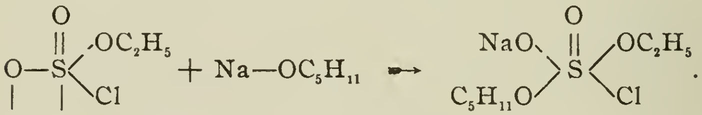
[1] Nef: Ann. Chem. (Liebig), **318**, 16, 40–50.

[2] Behrend: Ber. d. chem. Ges., **8**, 1004; Wold and Rüff: D. R. P., Kl. 17, 129,862. See Centrbl., 1902, I., 837.

Chlorsulphonethyl ester, therefore, in its reactions with ammonia, amines, alcohols, phenols, and their salts, does not act as such, *i. e.*, in the molecular form, but by virtue of its being partially dissociated into ethylidene, $CH_3CH=$, sulphur trioxide, SO_3, and hydrogen chloride, HCl.

There are two series of reactions of ethyl chlorsulphonate which must, however, be explained on the basis of an action between the non-dissociated molecules, $ClSO_2OC_2H_5$, and the reagents used; namely, those with sodium alcoholates in absolute ethereal solution and those with sodium malonic ester and allied compounds. In the former case Bushong has observed the formation of addition-products, soluble in ether, which are decomposed by heat or by addition of water. The addition-product of ethyl chlorsulphonate and sodium isoamylate described by Bushong was isolated by me in large quantity and found, contrary to his statement, to be remarkably stable. It can be boiled for hours under a reflux condenser, in absolute ethereal solution, without change if rigid precautions are taken to prevent an access of moisture. The waxy mass left after distilling off the ether does not, in fact, decompose until heated to 200° at 30 mm. pressure. In view of all this, it is highly improbable that the addition-product possesses the constitution given to it by Bushong,



$$O{-}\overset{O}{\overset{\|}{S}}\!<\!\begin{matrix}OC_2H_5\\Cl\end{matrix} + Na{-}OC_5H_{11} \longrightarrow \begin{matrix}NaO\\C_5H_{11}O\end{matrix}\!>\!\overset{O}{\overset{\|}{S}}\!<\!\begin{matrix}OC_2H_5\\Cl\end{matrix}.$$

This is now, in fact, the only reaction of ethyl chlorsulphonate which requires further investigation. It is the intention of Dr. Nef to study this addition-product with great care with the object of determining its constitution rigidly.

Ethyl chlorsulphonate, in view of the results with amines, alcohols, and phenols, was expected to react with the sodium salts of acetoacetic ester, malonic ester, and allied compounds in a manner entirely analogous to ethyl halides, ethyl nitrate, and diethyl sulphate,[1] *i. e.*, to give α-ethylacetoacetic ether, ethylmalonic ester, etc. This is, however, not the case. The substance acts here as a chlorinating agent, giving, for instance, α-chloracetoacetic ester and chlormalonic ester. Sulphurous acid and alcohol are the other products formed.

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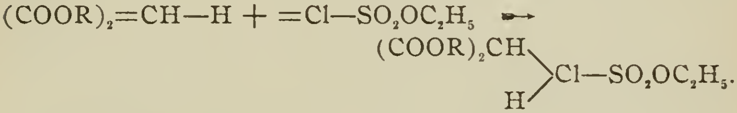
[1] Cf. "Behavior of Formhydroxamic Acid towards Acetone." Biddle: Ann. Chem. (Liebig), 310, 14.

This surprising and entirely unexpected result is due to the fact that the chlorine atom in the molecule of ethyl chlorsulphonate is unsaturated, and it therefore first absorbs the reagent,

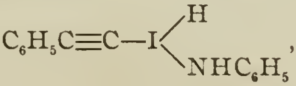


$$(COOR)_2{=}CH{-}H + {=}Cl{-}SO_2OC_2H_5 \longrightarrow \begin{matrix}(COOR)_2CH\diagdown \\ H\diagup\end{matrix} Cl{-}SO_2OC_2H_5.$$

The addition-product thus formed then dissociates into chlormalonic ester, $(COOR)_2CHCl$, and sodium ethyl sulphite, $Na{-}SO_2OC_2H_5$. The chlorinated malonic ester subsequently acts with the excess of sodium malonic ester present with formation of sodium chloride and acetylenetetracarboxylic ester.[2]

On further consideration these results are found to be entirely analogous to those obtained by Nef with sodium malonic ester and allied compounds in the case of cyanogen bromide and iodide as well as in the case of brom- and iodphenylacetylene, respectively.[3]

These reactions must obviously all be explained on a similar basis, and the isolation by Nef of an addition-product, iodphenylacetyleneanilide,



$C_6H_5C{\equiv}C{-}I\begin{matrix}\diagup H \\ \diagdown NHC_6H_5\end{matrix}$, justifies the interpretation of the reaction as given above.

The fact recently discovered by Brühl[4] that benzenesulphone chloride reacts with sodium camphorcarboxylic esters as a chlorinating agent, as well as the observation of Findeisen[1] that *p*-tolylsulphone chloride gives with sodium acetoacetic ester, *α*-chloracetoacetic ester, and sodium *p*-tolylsulphinate is naturally to be explained on an entirely analogous basis.

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[1] Nef: Ann. Chem. (Liebig), **309**, 186-188.

[2] Nef: *Ibid.*, **298**, 259.

[3] Nef: *Ibid.*, **298**, 260, foot-note; **308**, 299-316.

[4] Ber. d. chem. Ges., **35**, 4113.

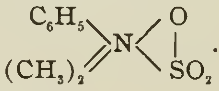
EXPERIMENTAL PART.

Preparation of Ethyl Chlorsulphonate.—The ethyl chlorsulphonate used in my work was prepared from sulphuryl chloride according to Bushong's modification of Behrend's method. It was found advisable to drop in the alcohol very slowly, to pass the current of air quite rapidly, and to dry the oil with anhydrous copper sulphate. By attending to these details the yield was raised to 80 per cent of the theory. Bushong states that the reaction-mixture separates into two layers, the lower consisting of ethyl chlorsulphonate. Although I have repeatedly prepared the substance in quantities of 200 grams, I have never been able to observe such a separation into layers.

Action of Chlorsulphonic Acid on Dimethylaniline.

The action of chlorsulphonic acid on dimethylaniline has such a significance for the chemistry of ethyl chlorsulphonate in its action with ammonia and amines that it is presented at this point.

Twenty-three grams of dimethylaniline, diluted with 80 cc. of chloroform, were placed in a quarter-liter flask and cooled by means of ice and salt. 19.5 grams of chlorsulphonic acid (0.5 molecule) were then slowly added by means of a dropping-funnel, the flask being constantly shaken. A granular precipitate appeared after the addition of the first few drops, and the interaction took place almost instantly. The precipitate was filtered, and washed with cold chloroform until it gave no test for chlorine ions. When freed from adhering chloroform on a porous plate, over sulphuric acid, in a vacuum, the precipitate consists of practically pure dimethylaniline-sulphurtrioxide,



$\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}\!>\!N\!<\!\begin{matrix}O\\|\\SO_2\end{matrix}$. The other reaction-product, phenyldimethylammonium chloride, is very soluble in chloroform and consequently is found, together with small quantities of dimethylaniline sulphurtrioxide, in the chloroform filtrate.

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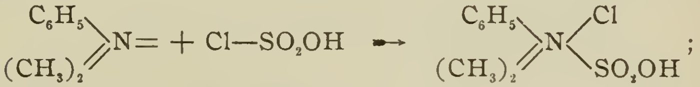
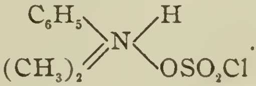
[1] J. prakt. Chem., [2], 65, 529.

The formation of these products, as discussed in the introduction, is self-evident on the basis of a partial dissociation of the chlorsulphonic acid molecules into sulphur trioxide and hydrogen chloride. The dissociated portions are then simply very rapidly absorbed by the excess of dimethylaniline molecules present.

Two other possible interpretations of the reaction have been carefully considered: I., the formation of an addition-product,



and II., of a salt-like compound,



Either of these hypothetical intermediate products must then be supposed to lose hydrogen chloride almost instantly at —15° and give the products actually obtained in the reaction under discussion. These interpretations, however, have not such inherent probability as the one adopted above. Williams'[1] vapor-density determinations of chlorsulphonic acid, at temperatures above 180°, show that the substance is partially dissociated into sulphur trioxide and hydrogen chloride. The vapor density of sulphuric acid at 400° proves that it is dissociated completely into sulphur trioxide and water at that temperature, and at 332° 34 per cent of the molecules of this acid are thus dissociated.[2] It is therefore self-evident that even at —15°, or at much lower temperatures, some molecules of chlorsulphonic acid are dissociated, equilibrium being maintained in the sense of the equation,

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[1] J. Chem. Soc. (London), [2], **7**, 304.

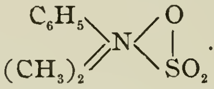
[2] Deville and Troost: Compt. rend., **56**, 891.

$$ClSO_2OH \rightleftarrows SO_3 + HCl;$$

addition of dimethylaniline must at once destroy this equilibrium and cause the reaction from left to right to proceed to completion.

According to Evans[1] the action of chlorsulphonic acid on dimethylaniline results in the formation of dimethylaniline-*p*-sulphonic acid, p-$(CH_3)_2N—C_6H_4SO_2OH$. This result is undoubtedly due to the fact that Evans took no precautions to prevent a rise of temperature on mixing his reagents. Dimethylaniline sulphur trioxide, which is the primary reaction-product, undergoes, on being heated to about 60°, a spontaneous transformation into the isomeric *p*-dimethylaniline-*p*-sulphonate (by intramolecular addition, see below).

Ethyl Chlorsulphonate and Dimethylaniline.

Dimethylanilinesulphurtrioxide,  $\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}\!\!>\!N\!<\!\begin{matrix}O\\|\\SO_2\end{matrix}$.—The action of ethyl chlorsulphonate on dimethylaniline has already been studied by Wenghöffer,[2] who obtained dimethylaniline-*p*-sulphonic acid and ethyl chloride as reaction-products,

$$C_6H_5N(CH_3)_2 + ClSO_2OC_2H_5 \rightarrow p\text{-}(CH_3)_2NC_6H_4—SO_2OH + C_2H_5Cl.$$

He obviously took no precautions to control the temperature on mixing his reagents, and consequently the intermediate formation of dimethylanilinesulphurtrioxide escaped his notice; furthermore, a large amount (20 per cent) of phenyldimethylethylammonium chloride is also formed in this reaction.

Fifty grams of dimethylaniline (2 molecules), diluted with an equal volume of chloroform, were thoroughly cooled by means of salt and ice; 30 grams of ethyl chlorsulphonate, similarly diluted, were then slowly added by means of a dropping-funnel, care being taken to shake vigorously during this operation. The reaction is practically completed as soon as all the ethyl chlorsulphonate has been added, and the white, granular precipitate of dimethylanilinesulphurtrioxide is filtered off, washed with chloroform, and dried on a clay plate. A very careful comparison with the precipitate obtained by treating dimethylaniline with chlorsulphonic acid, as described above, showed that the products are identical. Dimethylanilinesulphurtrioxide is somewhat soluble in chloroform, hence the yield is not quantitative; 34.5 grams of the product were obtained, which is 83.3 per cent of the theory. When dimethylanilinesulphurtrioxide is heated to about 60° it is transformed quantitatively into dimethylaniline-*p*-sulphonic acid: the equilibrium between the active and inactive dimethylanilinesulphurtrioxide particles (see below),

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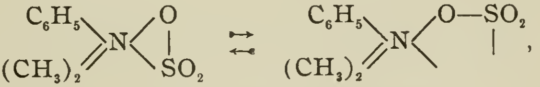
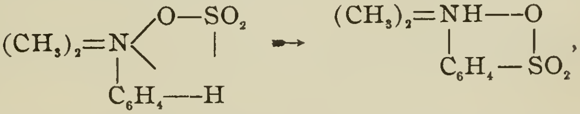
[1] Chem. News, 73, 53.

[2] J. prakt. Chem., [2], 16, 448.

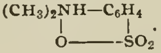


is finally disturbed at this temperature because of the fact that intramolecular addition,[1]



can take place (not reversible), and thus dimethylaniline-*p*-sulphonic acid, an ammonium salt, is quantitatively formed. A sample of dimethylaniline-*p*-sulphonic acid, thus prepared from dimethylanilinesulphurtrioxide by heat, gave the following figures for sulphur on analysis, by the Carius method:

0.3493 gram substance gave 0.3953 gram $BaSO_4$.

	Calculated for  $\begin{array}{l}(CH_3)_2NH—C_6H_4 \\ \quad\;\; | \qquad\quad | \\ \quad\;\; O———SO_2\end{array}$.	Found.
S	15.92	15.65

The sodium salt of this acid was also prepared and compared with the corresponding salt, made according to the directions in the literature.

The chloroform filtrate from the 34.5 grams dimethylanilinesulphurtrioxide was now worked up. Careful fractionation gave 9.9 grams of ethyl chloride (b. p. 12°), or 80 per cent of the theory. Further distillation, finally at reduced pressure, gave 19.7 grams unchanged dimethylaniline. The pasty residue now remaining in the distilling-flask consisted of ethyldimethylphenylammonium chloride and the dimethylaniline salt of dimethylaniline-*p*-sulphonic acid, which naturally must be formed by the action of heat on the dimethylanilinesulphurtrioxide which was dissolved in the chloroform.

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[1] Nef: Ann. Chem. (Liebig), 318, 33-35; cf. *Ibid.*, 298, 223-225.

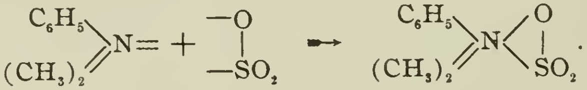
The tetraalkylated ammonium salt was obtained from this mixture by adding strong aqueous caustic soda, extracting the dimethylaniline thus set free by ether, and then neutralizing the aqueous solution with hydrochloric acid, and evaporating to dryness. The residue was then extracted with alcohol, and thus 7 grams of ethyl dimethylphenylammonium chloride were obtained. The chlorplatinate, which crystallizes from 80 per cent alcohol in beautiful yellow needles, was prepared and analyzed:

0.5059 gram substance gave 0.1408 gram Pt.

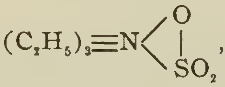
0.5980 gram substance gave 24 cc. N_2 at 20° and 750 mm. pressure.

	Calculated for $\left[\begin{matrix}C_6H_5\\C_2H_5\end{matrix}>N(CH_3)_2\right]_2PtCl_6$.	Found.
Pt	27.33	27.83
N	3.96	4.26

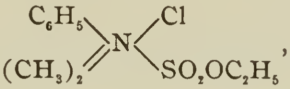
The results obtained in this experiment are in harmony with the conclusion that ethyl chlorsulphonate contains the following dissociated particles: I., ethylidene, $CH_3CH=$; II., sulphurtrioxide, SO_3; and III., hydrogen chloride, HCl. The sulphur trioxide combines with the dimethylaniline to give dimethylanilinesulphurtrioxide,



The hydrogen chloride is in part, 80 per cent, absorbed by the ethylidene, thus giving ethyl chloride, and is also in part, 20 per cent, taken up by the dimethylaniline present in excess, thus forming phenyldimethyl ammonium chloride. The latter substance is then immediately converted by the remainder of the available alkylidene into ethyldimethylphenylammonium chloride.[1]

Special experiments have shown, furthermore, that dimethylanilinesulphurtrioxide can also be prepared by cautious addition of sulphur trioxide to a well cooled solution of dimethylaniline in chloroform. The analogous compound, triethylaminesulphurtrioxide, , has in fact long been known, having been prepared by Beilstein and Wiegand[2] by mixing the two components in molecular proportions.

An interpretation of the reaction between dimethylaniline and ethyl chlorsulphonate on the basis of an intermediate formation of the addition-product,



which must then immediately break down at —15° into ethyl chloride and dimethylanilinesulphurtrioxide has also been carefully considered; it is *à priori* highly improbable in view of the properties of ethyl chlorsulphonate and chlorsulphonic acid. Furthermore, it is impossible to explain on this basis the fact that 20 per cent of ethyl dimethylphenylammonium chloride is formed in this reaction, since ethyl chloride and dimethylaniline do not combine under the conditions employed. Finally, this interpretation of the reaction is also excluded by the data obtained in the study of the reaction between ethyl chlorsulphonate and ammonia as well as diethylamine (see below).[1]

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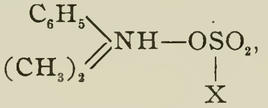
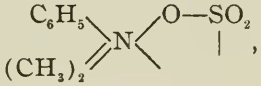
[1] Nef: Ann. Chem. (Liebig), **309**, 162–163.

[2] Ber. d. chem. Ges., **16**, 1264.

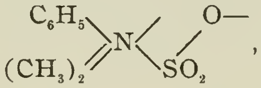
Properties of Dimethylanilinesulphurtrioxide. — Dimethylanilinesulphurtrioxide shows the properties of an unsaturated compound to a marked extent, absorbing water, alcohol, phenol, ammonia, primary and secondary amines, olefines, and acetone with great ease. In view of the fact that the resulting addition-products possess the general formula,



it must be concluded that the original compound possesses relatively the larger percentage of active A-molecules,



as compared with active B-molecules,



for instance.

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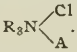
[1] The reaction taking place between tertiary amines and acyl chlorides, including chlorcyanogen, whereby acylated dialkylamines and alkyl chlorides,

$$R_3N + Cl{-}A \longrightarrow R_2N{-}A + RCl,$$

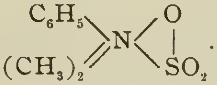
are formed [cf. Staedel: Ber d. chem. Ges., **19**, 1947; Braun: *Ibid.*, **35**, 1279], have been interpreted in the literature from the standpoint of an intermediate formation of the addition-product, .

There is, however, in view of my work [cf. Ann. Chem. (Liebig), **298**, 227, 269; **309**, 160–165; **318**, 182], another possible, and, as it seems to me, far more probable explanation of these reactions. A trisubstituted ammonia is partially dissociated at ordinary temperature into alkylidene and a secondary amine,

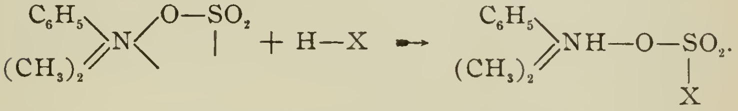
$$(C_nH_{2n+1})_3{\equiv}N \rightleftarrows C_nH_{2n}{=} + (C_nH_{2n+1})_2NH.$$

An analogous dissociation exists in the case of primary and secondary amines, but these need not be considered here. This explains why triethylamine gives acetaldehyde in the cold with aqueous permanganate [Claisen, Wallach: Ber. d. chem. Ges., 8, 1239], and why Hofman's reaction, as is well known, is reversible. In the reactions referred to, the acyl chloride therefore probably acts first with the dissociated tertiary amine particles, *i. e.*, with the secondary amine, to give the acylated secondary amine, and the hydrogen chloride thus formed is at once taken up by the alkylidene with formation of alkyl chloride. It is my intention to investigate these reactions in the near future with the object of testing experimentally the correctness of the views here presented. J. U. Nef.

These are naturally in equilibrium with the inactive molecules,



The addition of a reagent to dimethylanilinesulphurtrioxide therefore takes place exclusively[1] according to the scheme



The molecular rearrangement of the substance at 60° to dimethylaniline-*p*-sulphonic acid, mentioned above, is therefore also simply due to an intramolecular addition of the active A-molecules of dimethylanilinesulphurtrioxide.

Dimethylanilinesulphurtrioxide and Water.—Dimethylanilinesulphurtrioxide is very quickly acted upon by hot, but not so readily by cold, water; once moistened with water it is, however, impossible to prevent an action from setting in sooner or later. Freshly prepared dimethylanilinesulphurtrioxide can be washed with ice-water, spread out on a clay plate, and kept for some hours without apparent change. Eventually a spot of liquefaction will appear in the mass. Other spots then quickly appear and grow rapidly until, in a few seconds, the whole mass is transformed, with marked rise of temperature, into a liquid which, on cooling, solidifies to a mass of white crystals. The same phenomena are observed, after some time, when water and dimethylanilinesulphurtrioxide are brought together in molecular proportions at ordinary temperatures. The resulting crystalline product, when treated with aqueous sodium hydrate, gives, quantitatively, sodium sulphate and dimethylaniline. This fact, as well as the synthesis from equimolecular quantities of water and dimethylanilinesulphurtrioxide, identifies the addition-product as primary dimethylphenylammonium sulphate, $C_6H_5(CH_3)_2NHOSO_2OH$. The salt is very soluble in water and alcohol, and melts at 84° to 85°. Heated to 200° it is transformed, with loss of water, into dimethylaniline-*p*-sulphonic acid.

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[1] Cf. Nef: Ann. Chem. (Liebig), **298**, 204: **318**, 31; **335**, 198–199.

0.7214 gram substance gave 0.7890 gram $BaSO_4$.

	Calculated for $(CH_3)_2NH(C_6H_5)OSO_2OH$.	Found.
S	14.64	15.01

Dimethylanilinesulphurtrioxide and Alcohol.—Equimolecular quantities of dimethylanilinesulphurtrioxide and absolute alcohol unite, with marked evolution of heat, to give dimethylphenylammonium ethyl sulphate,

$$C_6H_5(CH_3)_2NHOSO_2OC_2H_5.$$

The salt solidifies, on cooling, to globular masses of radiating needles, melting at 54°. It is quite soluble in water and alcohol, and decomposes when heated to 200° with considerable charring. Treated with aqueous potassium hydrate, it gives dimethylaniline and potassium ethyl sulphate, thus establishing its constitution.

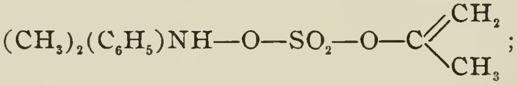
Dimethylanilinesulphurtrioxide and Acetone.—When dimethylanilinesulphurtrioxide is warmed gently with an excess of acetone the solid disappears, and there is a separation into two layers. The lower layer, on cooling, solidifies to a mass of large prismatic crystals, melting at 76° to 78°. The addition-product is soluble in water, but is decomposed both by acids and alkalies, giving acetone, sulphuric acid, and dimethylaniline.

1.1089 grams substance gave 1.000 gram $BaSO_4$.

	Calculated for $C_{11}H_{17}O_4NS$.	Found.
S	12.35	12.38

Two formulas are possible for this substance :

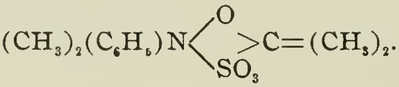
I.



$$(CH_3)_2(C_6H_5)NH{-}O{-}SO_2{-}O{-}C\left\langle\begin{matrix}{=}CH_2\\ {-}CH_3\end{matrix}\right. ;$$

and

II.



$$(CH_3)_2(C_6H_5)N\left\langle\begin{matrix}O\\ SO_3\end{matrix}\right\rangle C{=}(CH_3)_2.$$

An addition-product is also obtained by dissolving dimethylanilinesulphurtrioxide in warm malonic ester. On cooling, white leaflets are obtained which give, on treatment with aqueous alkali, malonic ester, sulphuric acid, and dimethylaniline.

Dimethylanilinesulphurtrioxide and Phenol.—When these two substances are brought together in molecular proportions they unite, with evolution of heat, to give dimethylphenylammoniumphenylsulphate, $C_6H_5(CH_3)_2NHOSO_2OC_6H_5$. This salt was obtained in the crystalline form. It is very soluble in water and is decomposed by aqueous potassium hydroxide, quantitatively, into dimethylaniline and potassium phenylsulphate. Consequently this is probably the easiest way to prepare the latter substance. An analysis of the potassium phenylsulphate obtained gave the following result:

0.4067 gram substance gave 0.1609 gram K_2SO_4.

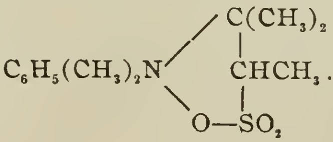
	Calculated for $C_6H_5OSO_2OK$.	Found.
K	18.39	17.73

The salt obtained was also compared very carefully with a preparation made according to the method of Baumann.[1]

Dimethylanilinesulphurtrioxide and Aniline.—These two substances unite very energetically when brought together in molecular proportions. A wax-like salt is formed which is decomposed by baryta water into dimethylaniline and barium phenylsulphamate, thus establishing the constitution as

$$C_6H_5(CH_3)_2NHOSO_2—NH.C_6H_5.$$

The sulphamate was identified by its reactions, and by comparison with the corresponding product obtained from aniline and ethyl chlorsulphonate (see below).

Dimethylanilinesulphurtrioxide and Trimethylethylene.—β-Isoamylene and dimethylanilinesulphurtrioxide unite with slight evolution of heat to form an indistinctly crystallized substance, obviously  $C_6H_5(CH_3)_2N\begin{cases}C(CH_3)_2 \\ \quad | \\ \quad CHCH_3 \\ \quad | \\ O—SO_2\end{cases}$.—It is decomposed by water into dimethylaniline, sulphuric acid, and amylene.

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[1] Ber. d. chem. Ges., 11, 1907.

The results here presented[1] suffice to show very clearly that dimethylanilinesulphurtrioxide is an excellent carrier of sulphur trioxide. They indicate an excellent means of preparing the monoalkylated sulphuric and sulphamic acids.

Ethyl Chlorsulphonate and Diethylamine.—Thirty-nine grams of diethylamine, diluted with 200 cc. absolute ether, were placed in a flask surrounded by ice and salt; 38 grams of ethyl chlorsulphonate (0.5 molecule), diluted with twice its volume of absolute ether, were added through a dropping-funnel. A white precipitate appeared at once and the odor of sulphonate was soon gone. Water was added until the precipitated salts had dissolved. The ether was separated from the aqueous layer, dehydrated with calcium chloride, and then distilled off on a water-bath. A small amount, 4 grams, of oily liquid remained, and this, on heating under reduced pressure to remove the last traces of ether, soon solidified. On crystallization from benzene colorless, orthorhombic prisms, melting at 89°, were obtained, which dissolve in water with a strongly acid reaction. The analysis and properties[2] prove that it is free diethylaminsulphonic acid,

$$(C_2H_5)_2N—SO_2OH.$$

0.3463 gram substance gave 29.8 cc. N_2 at 20° and 754 mm. pressure.

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[1] The interaction between sulphuric acid and alcohols, as well as ammonia and primary and secondary amines, which results, as has long been known, in the formation of primary alkyl sulphates and derivatives of aminosulphonic acid, respectively, $C_nH_{2n+1}.OSO_2OH$ and NH_2SO_2OH, must, in the light of the data here presented, be interpreted as follows: The alcohol, H—OR, or the amine, H—NR_2, is absorbed by the active sulphur trioxide molecules, $\underset{|}{O}—\underset{|}{S}O_2$, present at ordinary temperatures in sulphuric acid,

$$H_2SO_4 \rightleftarrows SO_3 + H_2O.$$

This explains why ether, which contains only a very small percentage of ethylidene particles at ordinary temperatures, but nevertheless decidedly more than ethyl alcohol, reacts only very slowly with concentrated sulphuric acid, in the cold, to give monoethylsulphuric acid. Ethyl alcohol, on the other hand, reacts at once, and with marked evolution of heat, with H_2SO_4, at ordinary temperatures, to form primary ethyl sulphate because it can add itself to the sulphur trioxide molecules present in the solution, whereas this is impossible in the case of ether. J. U. NEF.

[2] Behrend: Ann. Chem. (Liebig), **222**, 116.

0.4744 gram substance gave 0.7148 gram $BaSO_4$ (Carius).

	Calculated for $(C_2H_5)_2NSO_2OH$.	Found.
S	20.21	20.68
N	9.20	9.76

The aqueous solution, containing the main reaction-products, was now treated in a flask with an excess, 70 grams, of barium hydroxide, and finally heated in an oil-bath until the water, etc., had practically all distilled over. The distillate gave, on addition of solid caustic potash, and subsequent fractionation, 20 grams of basic oil boiling from 60° to 90°, and was, therefore, obviously a mixture of di- and triethylated ammonia. This oil, after thorough drying over solid potassium hydroxide, was diluted with an equal volume of absolute alcohol. Fifty grams of diethyl oxalate were added, and the mixture was then heated in a sealed tube, for four days, in a Kekulé water-bath.[1] The tube contents, on distillation, now gave 10 grams of triethylamine boiling at 90°. The chlorplatinate was prepared and analyzed :

0.2373 gram substance gave 0.0759 gram Pt.

	Calculated for $[(C_2H_5)_3NH]_2PtCl_6$.	Found.
Pt	31.89	31.87

The salt residue left in the flask after treatment with barium hydroxide and removal of volatile bases and water, was now powdered and treated with water and carbon dioxide, to get rid of the excess of barium hydroxide. The solution was then filtered, and evaporated to dryness on a water-bath. The residue, after further drying over sulphuric acid in a vacuum, was placed in a Soxhlet apparatus and extracted thoroughly with chloroform. The chloroform solution was found to contain 5 grams of an extremely deliquescent salt which answered in all respects to the properties of tetraethylammonium chloride. The chlorplatinate gave the following analytical data :

0.1498 gram substance gave 0.0443 gram Pt.

	Calculated for $[(C_2H_5)_4N]_2PtCl_6$.	Found.
Pt	29.23	29.55

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[1] Method of Duvillier and Buisine : Ann. chim. phys., [5], **23**, 289.

The residue left in the Soxhlet apparatus, undissolved by chloroform, was now digested for one hour with alcohol, whereupon only barium chloride remained undissolved. The alcoholic extract contained 30 grams of barium diethylsulphamate with some barium chloride. The latter was removed by dissolving the mixture in water, digesting with silver oxide, and subsequently treating with carbon dioxide, filtering, and evaporating to dryness. The barium salt is finally obtained in white needles.

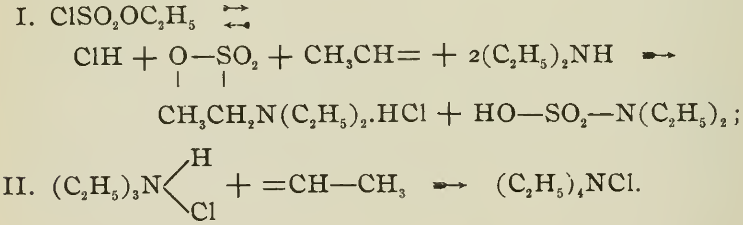
0.8811 gram substance gave 0.4258 gram $BaSO_4$.

0.5644 gram substance gave 0.9572 gram $BaSO_4$ (Carius).

0.9923 gram substance gave 21.1 cc. N_2 at 22° and 756 mm. pressure.

	Calculated for $[(C_2H_5)_2NSO_2O]_2Ba.2H_2O$.	Found.
Ba	28.78	28.44
S	13.40	13.55
N	5.86	6.06

The products formed in the action of ethyl chlorsulphonate on diethylamine are, therefore, diethylaminosulphonic acid and tri- and tetraethylated ammonium chlorides—*i. e.*, the diethylamine is both alkylated and sulphonated. In view of the facts presented in this paper this reaction must be interpreted as follows:



I. $ClSO_2OC_2H_5 \rightleftarrows$

$$ClH + \underset{|}{O}-\underset{|}{SO_2} + CH_3CH= + 2(C_2H_5)_2NH \rightarrow$$

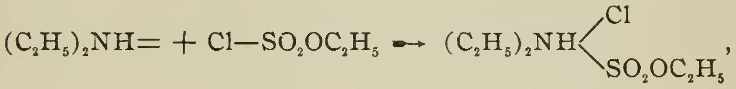
$$CH_3CH_2N(C_2H_5)_2.HCl + HO-SO_2-N(C_2H_5)_2;$$

II. $(C_2H_5)_3N\begin{matrix}/H\\ \backslash Cl\end{matrix} + =CH-CH_3 \rightarrow (C_2H_5)_4NCl.$

Diethylsulphamic Acid Ethyl Ester, $(C_2H_5)_2NSO_2OC_2H_5$.—It was first of all important to prove rigidly, by experiment, that diethylaminosulphone ethyl ester is not the intermediate product formed in the reaction between diethylamine and ethyl chlorsulphonate. This substance might be formed by the metathetical reaction,

$$(C_2H_5)_2NH + ClSO_2OC_2H_5 \longrightarrow (C_2H_5)_2NSO_2OC_2H_5 + HCl,$$

or through an intermediate formation of an addition-product, according to the equation,



$$(C_2H_5)_2NH{=} + Cl{-}SO_2OC_2H_5 \longrightarrow (C_2H_5)_2NH\left\langle\begin{matrix}Cl\\ SO_2OC_2H_5\end{matrix}\right.,$$

by subsequent loss of hydrogen chloride.

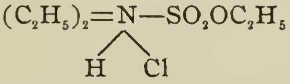
In view of the experiments of Nef with the alkylated sulphates, there was a strong possibility that diethylaminosulphone ethyl ester, $(C_2H_5)_2NSO_2OH + {=}CHCH_3$, provided it possesses a low point of dissociation, might in reality be the active alkylating agent in the reaction under consideration.

The same remarks hold good in the case of the interaction between ethyl chlorsulphonate and ammonia or aniline, *i. e.*, there is a possibility that aminosulphone ethyl ester or phenylaminosulphone ethyl ester, respectively,

$$NH_2{-}SO_2OC_2H_5 \qquad \text{or} \qquad C_6H_5NHSO_2OC_2H_5,$$

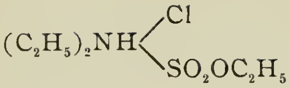
may really be the active alkylating agents in these instances.

This possibility was, however, rigidly excluded in the case of diethylamine by actually synthesizing diethylsulphamic ethyl ester. It is not an alkylating agent at ordinary temperatures (see below), nor does it give ethyl chloride by treatment in the cold with an excess of dry hydrogen chloride. Since it is, moreover, highly probable that by the latter treatment some molecules of



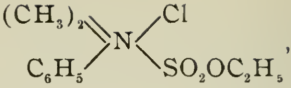
$$(C_2H_5)_2{=}\underset{H\quad Cl}{N}{-}SO_2OC_2H_5$$

must be formed, one must conclude that a substance of this character does not dissociate spontaneously into ethyl chloride and diethylsulphamic acid—an assumption which would have to be made in case the reactions of ethyl chlorsulphonate with di- and trialkylated amines were interpreted from the standpoint of an intermediate formation of the addition-products,



$$(C_2H_5)_2NH\left\langle\begin{array}{l}Cl\\ SO_2OC_2H_5\end{array}\right.$$

and



$$\left.\begin{array}{r}(CH_3)_2\\ C_6H_5\end{array}\right\rangle N\left\langle\begin{array}{l}Cl\\ SO_2OC_2H_5\end{array}\right.,$$

respectively. Finally, such an interpretation of these reactions is absolutely excluded in both cases because mixtures of a di- or a trialkylated amine and ethyl chloride do not interact perceptibly on one another at 0°.[1] The reactions of ethyl chlorsulphonate with ammonia, primary, secondary, and tertiary amines must, therefore, take place in the manner suggested above.

Diethylaminosulphone chloride, made according to the directions of Behrend,[2] was dissolved in absolute alcohol and treated with the theoretical amount of sodium ethylate; sodium chloride was deposited slowly. After two hours' standing the mixture was poured into water, and the oil which separated out was taken up in ether and dried with calcium chloride. The oil remaining, after distilling off the ether, had a yellow color and a disagreeable odor. On fractionating twice at reduced pressure diethylaminosulphone ethyl ester is obtained as a colorless, pleasant smelling oil boiling at 119° at 15 mm., and at 126° at 22 mm. pressure. Heated under atmospheric pressure, it decomposes with much charring.

0.3718 gram substance gave 0.4893 gram $BaSO_4$ (Carius).

0.3041 gram substance gave 19.8 cc. N_2 at 18° and 747 mm. pressure.

	Calculated for $C_6H_{15}O_3NS$.	Found.
S	17.67	18.00
N	7.73	7.40

Diethylsulphamic ethyl ester and diethylamine do not interact at ordinary temperatures when mixed in absolute ether solution. Dry ammonia is also without action under the same conditions. Consequently the substance does not act as an alkylating agent at 20° with ammonia or diethylamine; it cannot, therefore, be an intermediate product in the interaction between diethylamine and ethyl chlorsulphonate. The ester is, furthermore, recovered entirely unchanged when an ethereal solution has been saturated with dry hydrogen chloride. It was also not appreciably affected after twenty-four hours' standing with concentrated aqueous hydrochloric acid, in which it is insoluble. This indicates, therefore, that the substance is an exceedingly weak base or is entirely devoid of basic properties.

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[1] Cf. Menschutkin: Ztschr. phys. Chem., **5**, 589.

[2] Ann. Chem. (Liebig), **222**, 116.

Ethyl Chlorsulphonate and Ammonia.—The action of ethyl chlorsulphonate on ammonia has been studied by Baumstarck[1] and by Purgold,[2] but no decisive results were obtained. These reagents act with great violence on one another. The reaction must therefore be carried out in ether or benzene solution. The ethyl chlorsulphonate, diluted with ten times its volume of dry solvent, was cooled by means of ice and salt, and dry ammonia led in until the odor of the ester had disappeared. The main reaction-products are found in the deliquescent precipitate, which is filtered off and kept in a desiccator. The filtrate contained a small amount of material, the character of which varied with each experiment. In one case, using ether as a solvent, 2 cc. of triethylamine, boiling from 88° to 90°, were obtained. In another experiment, using the same solvent, 2 grams of a neutral, sweet-smelling oil containing nitrogen and sulphur were obtained. This gave, by hydrolysis with barium oxide, a barium salt soluble in water but insoluble in alcohol. Since the salt differed from barium diethylsulphamate, which is soluble in alcohol, and also was not identical with barium sulphamate, it was probably barium ethylsulphamate, and therefore the original oil must have been ethylaminosulphone ethyl ester. In a third experiment with ammonia and ethyl chlosulphonate, using benzene as a solvent, 3 grams of diethylaminosulphone ethyl ester, boiling at 117° to 119° at 15 mm. pressure, were obtained, identical in properties with the synthetic product described above. A nitrogen determination gave the following result :

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[1] Ztschr. für Chemie, 1867, p. 567.

[2] Ber. d. chem. Ges., **6**, 502.

0.2310 gram substance gave 14.9 cc. N_2 at 18° and 751 mm. pressure.

	Calculated for $C_6H_{15}O_3NS$.	Found.
N	7.74	7.42

As mentioned above, the main reaction-products (95 per cent) are insoluble in benzene or ether. One hundred grams of the dry precipitate were first extracted in a Soxhlet tube with chloroform; 18 grams of brown, syrupy salts were obtained, consisting of a mixture of di-, tri-, and tetraethylated ammonium chlorides. These were separated by digesting with an excess of aqueous barium hydroxide and subsequent distillation. The aqueous distillate gave, with caustic potash, etc., 6 grams of basic oil, boiling from 60° to 90°. It contained about equal parts of diethyl- and triethylamine, as determined by treatment with ethyl oxalate (see above). No ethylamine was found as a reaction-product. The residue left in the flask after water and volatile bases had been expelled gave, on extraction with chloroform, 7 grams of tetraethylammonium chloride. The chlorplatinate gave the following result on analysis:

0.2136 gram substance gave 0.0624 gram Pt.

	Calculated for $[(C_2H_5)_4N]_2PtCl_6$.	Found.
Pt	29.33	29.21

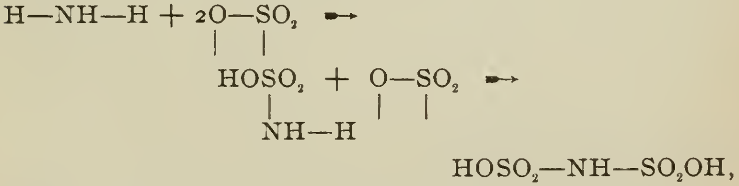
The original precipitate left in the Soxhlet apparatus, undissolved by chloroform, contains nothing which is soluble in alcohol. It dissolves in water with strongly acid reaction and gives a copious test for sulphate. The amount of sulphur removable from the precipitate as barium sulphate was determined quantitatively to be 11 per cent, whereas the total sulphur content by the Carius method was found to be 22 per cent. It is highly probable, from what follows, that the precipitate consists chiefly of ammonium chloride and ammonium imidosulphonate, $NH[SO_2ONH_4]_2$. The latter, on treatment with water, is split into equal molecules of sulphuric and aminosulphonic acids. The precipitate was first digested with an excess of aqueous barium hydroxide to expel the ammonia; carbon dioxide was then passed into the solution to get rid of excess of barium hydroxide. The filtrate now contained only barium chloride and barium sulphamate. The amount of chlorine in the solution was determined by titration, whereupon the calculated amount of silver sulphate was added in order to remove barium chloride. The filtrate, after treatment with carbon dioxide and hydrogen sulphide, was evaporated to dryness. The residue gave, on crystallization from dilute alcohol, 33 grams of pure barium sulphamate.

0.4784 gram substance gave 0.3121 gram $BaSO_4$.

	Calculated for $Ba(SO_3NH_2)_2$.	Found.
Ba	38.28	38.15

Treated with nitrous acid, in aqueous solution, the salt gives nitrogen and barium sulphate. Heated on a platinum foil, it gives white fumes, leaving a residue of barium sulphate.

The mechanism of the reaction between ammonia and ethyl chlorsulphonate is obviously analogous to the one taking place between this reagent and diethylamine. The ammonia is absorbed by the ethylidene, giving substituted ammonias, and these promptly take up hydrogen chloride to form salts which may also subsequently be further alkylated. Two molecules of sulphur trioxide must react with 1 molecule of ammonia to give imidosulphonic acid,



$$H{-}NH{-}H + 2\underset{|\quad\;|}{O{-}SO_2} \rightarrow \underset{NH{-}H}{\underset{|}{HOSO_2}} + \underset{|\quad\;|}{O{-}SO_2} \rightarrow HOSO_2{-}NH{-}SO_2OH,$$

which is then mainly converted into the ammonium salt.

Raschig[1] has shown that imidosulphonic acid is readily split by water into equal molecules of sulphuric and sulphamic acid, and this explains why imidosulphonic acid was not obtained, as such, in the experiments above described.

The fact that mono- and diethylated sulphamic ethyl esters, $C_2H_5NHSO_2OC_2H_5$ and $(C_2H_5)_2NSO_2OC_2H_5$, are occasionally formed in small quantities as reaction-products indicates the energetic alkylating properties of ethyl chlorsulphonate under the given conditions.

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[1] Ann. Chem. (Liebig), **241**, 178; cf. also Berglund: Ber. d. chem. Ges., **9**, 1896.

Ethyl Chlorsulphonate and Aniline.—The action of aniline on ethyl chlorsulphonate has been studied by Wenghöffer[1] and by Bushong.[2] The former obtained only sulphanilic acid and ethyl chloride as reaction-products. Shortly after the publication of Wenghöffer's paper, a preliminary notice by Wagner[3] appeared in which he stated that the formation of phenylsulphamic acid had been overlooked by Wenghöffer. Bushong observed the formation of ethylaniline in this reaction, and, citing the work of Wagner and Bamberger,[4] surmized that phenylsulphamic acid must also have been formed, but he apparently made no attempt to isolate the product.

In investigating this reaction I have found that when ethyl chlorsulphonate is added to aniline, without any attempt to control the decided evolution of heat, much ethyl chloride, as well as sulphanilic acid is formed ; if, however, the aniline is cooled by means of ice and salt not a trace of these products is obtained.

Eighty grams of aniline, diluted with absolute ether and well cooled, were treated with 62 grams of ethyl chlorsulphonate (0.5 molecule), also diluted with pure ether. The reaction-products were found exclusively in the precipitate which was filtered off and dissolved in water. The aqueous solution, as in the corresponding case with ammonia, was found to give a strongly acid reaction and to contain much sulphate. This latter is, undoubtedly, due to the hydrolysis of phenylimidodisulphonic acid, which must be split by water into equal molecules of sulphuric and phenylsulphamic acids.

The aqueous solution was therefore first digested with an excess of barium hydroxide, and the volatile bases carried over with steam and extracted by ether. Forty-seven grams of oil, boiling from 180° to 204°, were thus obtained. It consisted chiefly of a mixture of about equal parts of aniline and monoethylaniline. The oil gave, on treatment with nitrous acid in dilute aqueous hydrochloric acid solution, 24 grams of ethyl phenylnitrosamine.

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[1] J. prakt. Chem., [2], **31**, 1803.

[2] This JOURNAL, **30**, 223.

[3] Ber. d. chem. Ges., **19**, 1157.

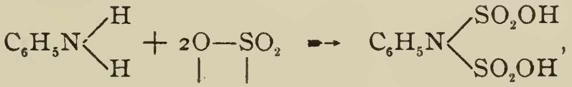
[4] *Ibid.*, **30**, 2275.

The solution from which the volatile bases had been removed was now worked up for barium phenylsulphamate in the following manner: It was first filtered from much barium sulphate, treated with carbon dioxide to get rid of excess of barium hydroxide, and then evaporated on a water-bath to incipient crystallization, taking care to add ammonia occasionally in order to keep the solution alkaline.[1] After recrystallizing twice from dilute ammonia water, 28 grams of pure barium phenylsulphamate were obtained, showing the following properties: It is hydrolyzed readily by boiling with dilute hydrochloric acid; on treatment with nitrous acid, barium sulphate and phenol are formed.

0.9753 gram substance gave 1.0086 gram $BaSO_4$ (Carius).

	Calculated for $Ba(OSO_2NHC_6H_5)_2$.	Found.
S	13.30	13.28

The reaction between aniline and ethyl chlorsulphate is consequently to be interpreted as follows: The ethylidene particles alkylate the aniline, giving chiefly ethylaniline[2] and only traces of higher alkylated products, and these unite at once with the hydrogen chloride to form salts. The sulphur trioxide (2 molecules) reacts with aniline to form phenylimidodisulphonic acid,



$$C_6H_5N\left\langle\begin{matrix}H\\H\end{matrix}\right. + 2\,\underset{|}{O}{-}\underset{|}{SO_2} \rightarrow C_6H_5N\left\langle\begin{matrix}SO_2OH\\SO_2OH\end{matrix}\right.,$$

and this, on treatment with water, is split into equal molecules of sulphuric and phenylsulphamic acids. From these data it is clear that aniline, on treatment in the cold with chlorsulphonic acid or with sulphur trioxide, must first give phenylimidodisulphonic acid. This is very probable from the following: Chlorsulphonic acid was allowed to act, at low temperatures, on a chloroform solution containing 3 or more molecules of aniline. The resulting precipitate, on treatment with aqueous barium hydroxide, gave large amounts of barium sulphate besides phenylsulphamic acid. Similar results are obtained when carefully prepared sulphur trioxide is added to an excess of aniline in the cold.

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[1] Traube: Ber. d. chem. Ges., **23**, 1653.

[2] Cf. Claesson and Lundvall: *Ibid.*, **13**, 1699.

Taking into consideration the fact that ethyl chlorsulphonate, chlorsulphonic acid, and sulphur trioxide all give, on treatment with aniline, phenylimidodisulphonic acid, or its products of hydrolysis, and that these reagents also give with dimethylaniline the same product, namely dimethylaniline sulphurtrioxide, we have in both instances a virtual demonstration of the presence of active sulphur trioxide particles.

The Action of Ethyl Chlorsulphonate on Alcohol and Sodium Alcoholates.

The action of ethyl chlorsulphonate on alcohol was one of the first reactions of this substance to be investigated. Some controversy arose as to the nature of the products formed, but it finally became evident that there are varying proportions of hydrogen chloride, ethyl chloride, ethyl ether, sulphuric acid, and primary and secondary ethyl sulphate. The formation of all these substances is now self-evident; the dissociation-products of ethyl chlorsulphonate—ethylidene, hydrogen chloride, and sulphur trioxide—must naturally act with the alcohol as follows: The sulphur trioxide adds the alcohol, giving primary ethyl sulphate, which is then partly converted by the ethylidene into diethylsulphate. The hydrogen chloride is in part absorbed by ethylidene, giving ethyl chloride, and some of the ethylidene naturally unites with the alcohol present in excess to give ether.

It must, however, be emphasized here that ethyl chlorsulphonate and sodium alcoholates give, in absolute ethereal solution, soluble and very stable addition-products, which were first observed by Bushong, and whose properties are discussed in the introduction. They are, moreover, as shown by Bushong, decomposed at once by addition of cold water, giving varying quantities of alkyl ethyl sulphate, alkyl sodium sulphate, sodium sulphate, alkyl ethyl oxide, and alkyl hydroxide.

Behavior of Ethyl Chlorsulphonate on Heating.

From the properties of ethyl chlorsulphonate described above, it follows that this substance must possess a very low point of dissociation.[1] This was found to be the case. When small quantities of ethyl chlorsulphonate are quickly distilled at ordinary pressure it boils approximately, but with noticeable decomposition, at about 152°. If, however, the substance is heated in a bath kept at 160°, decomposition sets in rapidly, as shown by what follows: Thirty grams of ethyl chlorsulphonate were placed in a flask with a long neck, which was connected in series with a Bunsen wash-bottle containing sodic hydroxide, a small tube containing bromine and water, and an azotometer. The flask was now heated in an oil-bath, the temperature of which was kept at 160°. The ester gradually darkened and evolved gas until only a tarry mass containing some free sulphuric acid was left. As soon as the air was expelled no bubble of gas passed beyond the bromine tube. The sodic hydroxide solution had gained 8.5 grams in weight, of which 6.2 grams increase was found to be due to absorbed hydrogen chloride (theory, 7.58 grams) and the remainder to sulphur dioxide. Seven and five-tenths grams of ethylene bromide, or 20 per cent of the theoretical amount, were found in the bromine tube.

Sulphur dioxide, sulphuric acid, ethylene (20 per cent), hydrogen chloride (80 per cent), and carbonaceous matter are therefore the products of decomposition of ethyl chlorsulphonate under the given conditions.

These results are self-evident from the standpoint of a dissociation into ethylidene, hydrogen chloride and sulphur trioxide, especially when one considers the experiments of Nef on the dissociation of alkyl sulphates, alkyl potassium sulphates, and alkyl haloids.[2]

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[1] Cf. Nef: Ann. Chem. (Liebig), 318, 40–50.

[1] *Ibid.*, 318, 1–57.

The sulphur dioxide results from the abstraction of oxygen from sulphur trioxide,

$$OSO_2 \rightleftarrows O + SO_2,$$

by ethylidene, and the resulting acetaldehyde is immediately polymerized and carbonized by more sulphur trioxide with formation of some sulphuric acid. Twenty per cent of the ethylidene is transformed, by intramolecular alkylation,[1] into ethylene.

Another experiment with 25 grams of ethyl chlorsulphonate was carried out in the presence of 20 grams of powdered tin and a trace of iodine. The apparatus was similar to that used in the former experiment, but a condenser and receiver were inserted between the caustic soda wash-bottle and the distilling-flask. On heating to 130°, ethylene, sulphur dioxide, and small amounts of hydrogen chloride were evolved and 4 cc. of tin tetrachloride were collected in the receiver. The stannic chloride was identified by its boiling-point and its chemical reactions.

This chlorination of the tin by the ethyl chlorsulphonate is easily understood because of the known properties of chlorsulphonic acid—which, as has been shown, is a dissociation-product of the ester.

Chlorsulphonic acid breaks down when heated in a sealed tube to 170° to 180°, giving equal molecules of sulphuric acid and sulphuryl chloride,[2]

$$2ClSO_2OH \rightarrow SO_2Cl_2 + SO_2(OH)_2.$$

More recently Wohl and Ruff[3] have shown that the same decomposition takes place at 70° in the presence of catalyzers, such as aluminium chloride, iodine chloride, etc. I have found that a chloroform solution of chlorsulphonic acid, containing traces of iodine, will dissolve metallic tin in the cold with brisk evolution of sulphur dioxide and formation of stannic chloride.[4] This reaction can also be explained on the basis of a dissociation of chlorsulphonic acid into sulphur trioxide and hydrogen chloride and subsequent decomposition of the hydrogen chloride by the stannous chloride with formation of stannic chloride and atomic hydrogen, which is at once absorbed by the sulphur trioxide molecules present to give sulphur dioxide and water. It does not, therefore, necessarily involve an intermediate transformation of chlorsulphonic acid into equal molecules of sulphuric acid and sulphuryl chloride.

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[1] Nef: Ann. Chem. (Liebig), 318, 13.

[2] Behrend: Ber. d. chem. Ges., 8, 1004.

[3] *Loc. cit.*

[4] Cf. Heumann and Köhlin: Ber. d. chem. Ges., 15, 416.

Ethyl Chlorsulphonate and Sodium Acetoacetic Ester.

The reaction of ethyl chlorsulphonate with the sodium salt of malonic ester and acetoacetic ester, respectively, has already been referred to in the introduction; contrary to expectation, no alkylation takes place. The ethyl chlorsulphonate acts as a chlorinating agent in both cases. Similar results have been observed previously by Nef in the case of cyanogen bromide and iodide, as well as in the case of brom- and iodphenylacetylene. Analogous results have also since been obtained by Brühl with benzenesulphonechloride and by Findeisen with *p*-tolylsulphone chloride. There is no doubt that carbon tetrachloride, bromide, and iodide, as well as all nitrogen halogen compounds, will give similar results on treatment with sodium malonic ester and allied compounds. The theory of the reaction has been exhaustively discussed by Nef[1] and is briefly presented in the introduction.

To 58.8 grams of sodium acetoacetic ester, suspended in absolute ether, and cooled in a freezing-mixture, 26.7 grams of ethyl chlorsulphonate (0.5 molecule) were added. The reaction takes place quietly. After two hours' standing the ether was decanted, and the sticky precipitate removed, and well washed by kneading with ether in a mortar.

The ether was found to contain 33 grams of oil, which consisted of about equal parts of acetoacetic ester and α-chloracetoacetic ester, besides small amounts of diacetsuccinic ester. These were separated by shaking with cold 10 per cent sodium carbonate solution by which only the α-chloracetoacetic ester is dissolved. It is then recovered from the alkaline solution by acidifying with dilute sulphuric acid and extracting with ether. The sticky precipitate, insoluble in ether, was dissolved in water and found to contain some soluble sulphate, besides a large amount of sulphite and alcohol; the residue therefore consisted chiefly of sodium ethyl sulphite with some sodium sulphate.

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[1] Ann. Chem. (Liebig), 308, 301–307.

Copper acetoacetic ester and ethyl chlorsulphonate do not react at ordinary temperatures in benzene solution. On heating the mixture under a reflux condenser, cuprous chloride is gradually formed. The filtrate, after getting rid of benzene, gave a dark, sticky, non-volatile gum, from which it was impossible to isolate a definite product.

Ethyl Chlorsulphonate and Sodium Malonic Ester.—Fifty-seven grams of sodium malonic ester, suspended in cold absolute ether, were treated with 22.5 grams of ethyl chlorsulphonate (0.5 molecule). The reaction takes place rapidly but without marked rise in temperature. The mixture was heated for a short time on a water-bath and the ether then poured off from the sticky precipitate, which was handled as in the case of sodium acetoacetic ester. The ether solution gave, on fractionation under reduced pressure, 8 grams of malonic ester and 20 grams of a snow-white solid. The latter, on crystallization from ligroin, was identified as acetylene-tetracarboxylic ester, $(COOR)_2CH—CH(COOR)_2$, melting at 75° and boiling at 205° to 208° under 42 mm. pressure. It was carefully compared with a known sample kindly loaned me by Dr. Nef.

The sticky precipitate, 31.5 grams, insoluble in ether, was found to contain only traces of sulphate. It obviously contained chiefly sodium chloride and sodium ethyl sulphite. The main portion was treated with dilute sulphuric acid when much sulphur dioxide was set free. The solution, which contained no perceptible amount of malonic ester, was distilled, and the first portions of the distillate gave, on treatment with solid potassium carbonate, 2 cc. of ethyl alcohol, which was identified by conversion into ethyl benzoate.

The Reactions of Ethyl Hypochlorite.

Finally, it may be of interest to state in this connection that very careful experiments with large amounts of ethyl hypochlorite and sodium ethylate, using dry ligroin as a diluent, have shown that reaction takes place almost instantly at 0°, but no trace of ethyl ether[1] or of diethyl hyperoxide is formed.

According to the observations of Bushong, made while in this laboratory, ethyl hypochlorite acts with sodium phenolate and sodium acetoacetic ester as a chlorinating agent. The same is true, as I have found, in the case of diethylamine and trimethylethylene, *i. e.*, chlordiethylamine, $(C_2H_5)_2NCl$, and chlorisoamylene, besides ethyl alcohol, are formed.

These observations, therefore, show that ethyl hypochlorite does not act here as an alkylating but as a chlorinating agent; the latter property is naturally to be explained on the same basis as the reactions of ethyl chlorsulphonate just presented.

Ethyl Chlorsulphonate and Sodium Phenolate.—In view of the striking analogy often existing between the reactions of sodium acetoacetic ester and those of the sodium salts of phenols, it seemed of especial interest to determine whether ethyl chlorsulphonate would behave towards sodium phenolate as a chlorinating or as an alkylating agent. The experiment was carried out and the reaction found to be analogous to those obtained with free alcohols and with sodium alcoholates, *i. e.*, only alkylation takes place.

The action of ethyl chlorsulphonate on phenol has been mentioned by Purgold,[2] who, however, obtained no definite results.

Fifty grams of dry sodium phenolate, prepared by mixing alcoholic solutions of carbolic acid and sodium ethylate, and distilling off the alcohol in an atmosphere of hydrogen, were finely powdered, suspended in absolute ether, and cooled with ice-water. Thirty-one grams of ethyl chlorsulphonate (0.5 molecule) were thereupon added, and the mixture shaken until the odor of the ester had disappeared. The salt residue, insoluble in ether, weighed 31 grams and was found to contain 29.1 per cent of sodium, 20 per cent of chlorine, and 15.76 per cent of sulphur (precipitated as barium sulphate). It gave a strongly acid reaction and obviously consisted only of sodium chloride and primary sodium sulphate. The ether solution gave 46 grams of oil, which, by separating with aqueous sodic hydrate, was proved to consist of 22 grams of phenetol, $C_6H_5OC_2H_5$, and 24 grams of carbolic acid. The phenetol boiled at 172° and, by heating in a sealed tube with hydriodic acid, was decomposed into ethyl iodide and phenol.

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[1] Cf. Nef: Ann. Chem. (Liebig), **298**, 323-324; **318**, 47-48.

[2] Ber. d. chem. Ges., **6**, 502.

In conclusion, I take great pleasure in gratefully acknowledging my obligations to the inspiring example and advice of Dr. Nef in the prosecution of this work.

USE OF THE CHROMATES OF BARIUM AND OF SILVER IN THE DETERMINATION OF SULPHATES AND CHLORIDES.

By Launcelot W. Andrews.

Several years ago a method was described by the author[1] for the volumetric determination of sulphates, of which the leading features may be recalled in outline here. A reagent, prepared by dissolving barium chromate in dilute hydrochloric acid, was added to the sulphate solution, the liquid was then neutralized, and, after filtration, the chromate in the filtrate titrated iodometrically in the usual manner. The amount of chromate so found was equivalent to the sulphate originally present.

This process is both accurate and rapid, as shown by my own observations and those of others.[2] It suffers, however, from a rather serious drawback, namely, that a solution of barium chromate in hydrochloric acid of the prescribed concentration does not keep perfectly,[3] a fact overlooked at the time of the publication of my first paper referred to above,

[1] This Journal, **11**, 567 (1889).

[2] Marchlewski: Fres. Ztschr. **32**, 316 (1893); Reuter: Chem. Ztg., **22**, 357 (1898); compare also Stolle: Ztschr. angew. Chem., 1892, p. 234.

[3] A. von Asboth: Chem. Ztg., **16**, 922 (1892).

owing to the fact that I had not then had occasion to work with solutions which had been kept more than ten days. Hydrochloric acid is, nevertheless, gradually oxidized by chromic acid, even in solutions far more dilute than the weakest which could be practically used for dissolving barium chromate, although weeks, months, or years may be requisite to make the action very apparent.

To overcome this difficulty, which has doubtless stood in the way of a more general employment of the method in question, it is obviously necessary to substitute for the hydrochloric acid some other acid which will not be capable of oxidization by chromic acid, which will not itself be either an oxidizing or a reducing agent in its action on hydriodic or chromic acids, and which will be sufficiently strong to dissolve the requisite amount of barium chromate. As possessing these qualifications two acids come into consideration in the first rank, *i. e.*, trichloracetic and perchloric acids. The latter would probably be extremely well suited to the purpose, but it cannot, at present, be obtained by purchase in a sufficiently pure state, that is, free from hydrochloric acid and from all lower acids of chlorine.

Trichloracetic acid meets all requirements as to resisting the action of chromic acid, and it can be purchased in the pure state without trouble. A normal solution of this acid is capable of dissolving the finely divided barium chromate rather freely but not very rapidly. The solution may be aided by the application of gentle heat, but caution must be observed in this direction in order to avoid too extensive hydrolysis. Thus, a normal solution of trichloracetic acid was agitated with an excess of barium chromate at about 90° for a few minutes, free evolution of carbon dioxide and chloroform occurring. The liquid was then cooled and allowed to stand for three days at the temperature of the room.

A slight recrystallization of the barium chromate had taken place. The liquid now contained in each cubic centimeter 126 milligrams of trichloracetic acid and 24 milligrams of barium chromate. On further standing, an increased deposition of the chromate was observed. For practical purposes it may be assumed that in concentrations between normal and seminormal, trichloracetic acid is capable of maintaining permanently in solution one-sixth of its own weight of barium chromate. Observations on this solution have now continued six months and no change has been noted that in any way influences the analytical results obtained with it. Of course, the hydrolysis of the trichloracetic acid goes on, but this change is slow and has absolutely no bearing, since the solution is not employed as a standard and is always used in excess.

This modification entirely does away with the only objection to the method in its original form. No other change is required beyond the substitution of trichloracetic for hydrochloric acid, so that for all details reference may be made to the former paper (*loc. cit*).

Since the question of priority has been raised concerning the original method as between myself and Quantin, I desire to state what the facts are that bear on the history of the process. My method was described in a paper read before the Iowa Academy of Sciences in Des Moines, Dec. 27, 1887,[1] which was published in this JOURNAL in 1889.[2] Quantin published in 1889[3] a somewhat similar process, of which the following are the features: Equal volumes of equivalent standard solutions of potassium dichromate and of barium chloride are mixed with sufficient hydrochloric acid to keep the barium chromate from separating. This liquid is added to the sulphate solution, then ammonia to alkaline reaction, and, after filtration, the chromate in solution is titrated by standardized ferrous sulphate, using potassium ferricyanide as indicator of the end of the reaction. Quantin had previously published practically the same method in 1886.[4] It will be seen that Quantin's method differs from mine not only in the choice of titration by ferrous solution, but in the far more important particular that two or three[5] titrated solutions are demanded by his process, whereas only one is used in mine, because in the latter the proper relation between barium and chromic acid is secured by starting with pure barium chromate instead of placing dependence upon a preliminary analytical process to secure this end. Hence the former method always demands a correction, variable in each case. Naturally, if I had been aware of Quantin's publications I would not have omitted to mention them, but at the time his second paper had not reached this country and his first was not mentioned in publications available to me. As a matter of fact, the only points in common to the essentially different methods is that both make use of barium and of chromic acid salts.

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[1] The proceedings of this meeting were not published till 1890.

[2] *Loc. cit.*

[3] Bull. soc. chim., [3], **1**, 21 (1889).

[4] Moniteur scientifique, 1886, p. 1222; also reprinted in Chem. News, **54**, 233.

[5] Two in the modified, three in the first process (1886).

It appears as if the principle, peculiar to my method, of using a reprecipitable salt is capable of more extended application, as for instance to the determination of chlorides. Thus, if silver chromate is added to a solution of a chloride, an equivalent amount of chromate passes into solution in accordance with the equation

$$2MCl + Ag_2CrO_4 = M_2CrO_4 + 2AgCl,$$

and a colorimetric or volumetric[1] titration of the chromate allows a conclusion as to the amount of the chloride, bromide, etc., originally present. The feasibility of this scheme has been tested under my direction by Mr. H. V. Farr, who has obtained excellent results. A new volumetric method for determining chlorides is hardly a desideratum, perhaps, but a good colorimetric method for estimating traces of chlorides, as for example, in water analysis, cannot be regarded as superfluous. The experiments have demonstrated that it is not necessary to bring the silver chromate into solution by any acid. It is sufficient to agitate the finely divided and carefully prepared salt with the highly dilute chloride solution, then to filter or decant, and compare the depth of color of the clear liquid with that of a suitable series of types made by dissolving known amounts of potassium monochromate in water. These type solutions keep indefinitely. The process is much more rapid than any titration method, and for the most dilute solutions is at least as accurate. It is expected to follow this preliminary notice of the method by a more detailed account.

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[1] Compare De Konninck and Niboul: Ztschr. f. angew. Chem., 1891, p. 295.

CHEMICAL LABORATORY,
STATE UNIV. OF IOWA,
July 13, 1904.

Contributions from the Chemical Laboratory of the University of Cincinnati.

METHODS FOR THE DETECTION OF ACETATE, CYANIDE, AND LITHIUM.

BY STANLEY R. BENEDICT.

A method for the detection of acetates, much more delicate than those in common use, or than any of which I have been able to find record, can be based upon the two well-known facts (1) that unlike most weak acids, acetic acid has a soluble silver salt, and (2) that the acidity or degree of ionization of acetic acid is greatly reduced by the presence of an acetate.

The solution, freed from all cations except those of the sodium group, is made just alkaline with sodium carbonate. An excess of silver nitrate solution is now added and the precipitate filtered off, the solution being thus left perfectly neutral. The excess of silver is removed with a little normal sodium chloride solution. The filtered solution is now saturated with hydrogen sulphide.

In another test-tube 2 cc. normal cobalt nitrate are acidulated with 2 or 3 drops normal acetic acid and saturated with hydrogen sulphide. A small amount of cobalt sulphide will usually be precipitated, but may be disregarded.

Upon mixing the two solutions thus prepared a heavy black precipitate of cobalt sulphide will be obtained immediately if the test solution contains acetate. This test is capable of detecting acetate in a N/500 solution of sodium acetate. It is applicable in presence of all strong acids and of all weak acids having insoluble silver salts.

The following method for the detection of cyanides in presence of sulphocyanates and ferrocyanides is reliable and extremely delicate. It has the advantage over the best methods hitherto proposed of avoiding the somewhat cumbersome expedient of distillation. It is based upon the action of cyanides upon the freshly precipitated oxides of mercury. As the method was first worked out, a solution of a mercuric salt was made alkaline with sodium hydroxide and the solution to be tested was added. It was found that in presence of cyanide the yellow precipitate of mercuric oxide dissolved (presumably with formation of a complex cyanide). Neither sulpho- nor ferrocyanides show this solvent action upon mercuric oxide.

The solvent action of cyanides is so marked that a portion of the precipitate formed, upon treating 1 cc. of N/25 mercuric chloride solution with sodium hydroxide, can be seen to dissolve when treated with a few cubic centimeters of a N/2000 solution of potassium cyanide. Of course, the full delicacy of the test could best be secured by filtering off any precipitate remaining after adding the solution to be tested, acidifying the filtrate, boiling, and testing for mercury with hydrogen sulphide.

It has, however, been found, that the action of cyanides upon mercurous oxide can be made the basis of a more delicate and desirable test than the one above proposed.

If a solution of mercurous nitrate be precipitated with an excess of sodium hydroxide, and potassium cyanide solution then be added, a portion of the precipitate dissolves, while the color of that which remains is changed from black to light gray. The action of the cyanide is to cause a portion of the mercurous oxide to be reduced to metallic mercury with the formation of a corresponding amount of mercuric oxide, which is then dissolved by the cyanide present. The gray precipitate remaining can readily be shown to be metallic mercury. Vitali[1] showed that hydrocyanic acid has this action upon calomel and some other mercurous salts. The mercurous oxide is in nowise affected by either ferrocyanides or sulphocyanates. In order to obtain the full delicacy of the test it should be made as follows:

The solution to be tested is made alkaline with sodium hydroxide, then about 0.5 to 1 cc. of N/25 mercurous nitrate is allowed to flow slowly down the side of the tube so that it will remain upon the top. A ring of black mercurous oxide is thus formed. The test-tube is now gently agitated so that a mixture of the precipitate with the solution slowly takes place. If cyanide be present, a portion of the precipitate will dissolve while the rest will become light gray in color.

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[1] O. Vitali: L'Orosi, **15**, 186; J. Chem. Soc., **62**, 1416 (1892).

When made as above described this test is extremely delicate, readily detecting CN in 5 cc. of a solution containing about 1 part CN in 1,000,000 parts of solution. This is not the limit of its delicacy. When it is remembered that the limit of the Prussian blue test for cyanide is placed by Link and Moeckel[1] at 1 part in 50,000, it will be seen that this test is not at all lacking in delicacy.

When the test is made, not by the contact method as described but by simply adding the mercurous nitrate to the alkaline test solution, there is a possibility, when the proportion of mercurous nitrate used is small, of mistaking the small quantity of black mercurous oxide, distributed through the liquid, for the gray mercury, whose formation constitutes the test, but no such confusion can arise if the above directions are adhered to. For the most delicate work a blank test with pure sodium hydroxide may be made for comparison, the same proportions of mercurous nitrate and sodium hydroxide being used as in the test.

While ferricyanides would interfere with this test, it will be remembered that cyanides are oxidized by these, so that it is unnecessary to test for cyanides when ferricyanides are present.

The detection of lithium in the presence of sodium without the aid of the spectroscope is attended with considerable difficulty. Of the precipitation methods so far proposed, practically only one can be of any service, *viz.*, the precipitation as phosphate in alkaline solution. Yet this method, as hitherto proposed, can be applied only where lithium is present in considerable amount, say not less than a N/8 solution. By the modification of this method described below, it is possible to obtain a distinct precipitate with a N/100 solution of lithium chloride, this being about the limit of its availability. This modification depends upon the fact that the precipitate of lithium phosphate is much less soluble in dilute alcohol (whether hot or cold) than in water, while sodium phosphate, although precipitated by dilute alcohol, readily redissolves upon heating. The procedure is as follows: A little ammonium hydroxide is added to the solution to be tested, then about one-tenth volume of N/5 disodium hydrogen phosphate is added, and finally enough ethyl alcohol to produce a fairly heavy precipitate, which remains permanent upon shaking the tube. This precipitate may consist of only sodium phosphate, or may be a mixture of sodium phosphate and lithium phosphate. The solution is now heated to boiling. If lithium be absent the precipitate will completely dissolve, leaving a perfectly clear solution; if, however, lithium be present it will be precipitated upon warming, and the precipitate will not dissolve even upon hard boiling. If the amount of lithium be small the solution will first clear and the precipitate will form upon boiling. Salts of potassium and ammonium do not interfere.

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[1] Link and Moeckel: Ztschr. anal. Chem., **17**, 456 (1878).

ON THE RATE OF CRYSTALLIZATION OF PLASTIC SULPHUR.

By J. H. Kastle and Walter Pearson Kelley.

The fact that plastic sulphur gradually changes into the crystalline variety of the element has been known for a long time. According to Dumas[1] this change usually requires from twenty-four to thirty-six hours. It has also been observed to vary with the temperature. According to Regnault[2] the change is so rapid at 100° that the thermometer shows a rise of temperature of from 10° to 12°. According to Daguin[3] the crystallization of plastic sulphur always begins in the center of the mass or in the axis of the cylinder, that is, at the point where the cooling has been slowest. He concludes, therefore, that the more rapid the cooling of the sulphur the slower the crystallization. He also observed that sunlight greatly accelerates the rate of crystallization, and that the higher the temperature at which the sulphur had been poured the slower its conversion into the crystalline modification.

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[1] Ann. chim. phys., [2], **36**, 83 (1821).

[2] *Ibid.*, [3], **1**, 205 (1841).

[3] Compt. rend., **20**, 1665 (1845).

According to Deville[1] plastic sulphur is a mixture of sulphur which is soluble in carbon bisulphide and an insoluble variety. In one specimen of plastic sulphur he found 35 per cent of the insoluble form. This insoluble portion he found to be remarkably stable at ordinary temperatures, showing no tendency to crystallize even after four years. On the other hand, when heated to 100° it soon changed to the crystalline variety. More recently Gernez[2] made a study of the rate of change of supercooled sulphur into the crystalline varieties. His method consisted in fusing octahedral sulphur in a graduated U-tube of 2 mm. bore, at a definite temperature, and for a certain definite length of time. The tube containing the fused sulphur was then immersed in a bath, the temperature of which was below the melting-point of sulphur. A small crystal of prismatic or octahedral sulphur was then dropped into the U-tube and the time required for the solidification of the sulphur through a constant distance of 10 mm. determined. It was found that sulphur that had been heated to 170° required a considerably longer time for solidification than that which had been fused at lower or higher temperatures. According to this observer this is in harmony with the observations of Berthelot, who found that at 170° the greatest amount of insoluble sulphur is produced. Gernez also observed that the phenomena attending the solidification of supercooled sulphur are more complicated than in the case of phosphorus, the difference being probably due to the fact that amorphous phosphorus is insoluble in the fused ordinary variety, whereas the different modifications of sulphur remain mixed together in the fused mass.

Several years ago the attempt was made by Mr. H. P. Bassett[1] and one of us (Kastle) to determine the rate of change of plastic sulphur into the crystalline variety, by determining the amount of soluble and insoluble sulphur remaining in certain specimens of plastic sulphur at the end of certain intervals after its preparation. The method was not found to lend itself particularly well to these determinations, however, and the attempt was abandoned. Later it occurred to us that more reliable results might possibly be obtained by the specific gravity and dilatometric methods. The results of these measurements are given in the following pages:

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[1] Compt. rend., **26**, 119 (1848).

[2] *Ibid.*, **95**, 1278-1280; **97**, 1298-1301, 1366-1369, 1433-1435, 1477-1480; **98**, 144-146; **100**, 1584-1585.

Experiment 1.

Sulphur heated to 200° and poured into cold water. The specimen was then kept in water, at ordinary temperature, during the several intervals indicated below:

	Grams.	Specific gravity.[2]	Per cent changed.
Weight in water when poured	2.144	1.923	0
" " " 1 hour later	2.168	1.943	15.7
" " " 1 " "	2.192	1.963	31.4
" " " 3 hours "	2.2038	1.973	39.2
" " " 4 " "	2.2125	1.981	45.6
" " " 5 " "	2.2195	1.987	50.3
" " " 6 " "	2.2252	1.992	54.3
" " air	4.4665		

Another specimen of the same pouring was kept in water at 70° for certain intervals indicated below, with the following results:

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	2.249	2.021	77.1
Weight in water after being heated 2 hours	2.261	2.032	850.
Weight in water after being heated 3 hours	2.262	2.33	86.6
Weight in water after being heated 4 hours	2.270	2.04	92.1
Weight in water after being heated 5 hours	2.275	2.045	96.0
Weight in air	4.451		

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[1] Thesis for the degree of B. S., 1901.

[2] The specific gravity of the sulphur was determined in every case by weighing the specimen, suspended by a fine silk thread, in a beaker of distilled water at ordinary temperatures.

Experiment 2.

Another experiment was carried out with sulphur which had been heated to 444° before pouring. One portion of this specimen was heated to 80°, another to 60°, and another to 40°. The one heated to 80° showed the following results :

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	0.8328	2.935	76.7
Weight in water after being heated 2 hours	0.8395	2.039	79.1
Weight in water after being heated 4 hours	0.8465	2.07	100.0
Weight in air	1.6373		

The specimen heated to 60° showed the following :

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	1.7425	1.958	25.0
Weight in water after being heated 2 hours	1.7477	1.964	28.8
Weight in water after being heated 4 hours	1.756	1.973	34.9
Weight in air	3.5602		

The specimen heated to 40° showed the following :

	Grams.	Specific gravity.	Per cent changed.
Weight in water after being heated 1 hour	2.1275	1.936	11.6
Weight in water after being heated 2 hours	2.1603	1.944	33.3
Weight in water after being heated 4 hours	2.1838	1.985	49.6
Weight in air	4.3992		

The initial specific gravity of the sulphur used in Experiment 2 was found to be 1.921.

Experiment 3.

In this experiment the sulphur was heated to boiling and poured at 444° into cold water. The specimen was then kept under cold water for certain intervals, at the end of which the specific gravity was determined with the following results :

	Gram.	Specific gravity.	Per cent changed.
Weight in water when poured	0.4425	1.952	0
" " " 1 hour later	0.449	1.979	25.0
" " " 2.5 hours later	0.457	2.015	58.3
" " " 5 " "	0.463	2.042	83.3
" " " 6.5 " "	0.465	2.051	91.6
" " " 7.5 " "	0.466	2.056	96.3
" " " 24 " "	0.467	2.06	100.0
" of sulphur in air	0.9072		

Experiment 4.

Conditions similar to those in Experiment 3.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7841	1.947	0
" " " 6 hours later	0.7841	1.947	0
" " " 7.5 " "	0.7868	1.955	11.1
" " " 8.5 " "	0.791	1.965	25.0
" " " 11 " "	0.8021	1.992	62.5
" " " 12 " "	0.805	1.999	72.2
" " " 24 " "	0.8129	2.019	100.0
" " air	1.6105		

Experiment 5.

Conditions same as in Experiments 3 and 4.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7325	1.919	0
" " " 3 hours later	0.7325	1.919	0
" " " 4.5 " "	0.7344	1.923	3.2
" " " 28 " "	0.746	1.952	26.4
" " " 30 " "	0.7596	1.986	53.6
" " " 31.5 " "	0.7646	1.999	64.0
" " " 33 " "	0.7708	2.015	76.8
" " " 35 " "	0.774	2.024	84.0
" " " 51 " "	0.7813	2.044	100.0
" " air	1.5295		

These results undoubtedly indicate that the rate of change of plastic into crystalline sulphur varies according to the temperature at which the sulphur is poured; in other words, it diminishes with the degree of the supercooling, and also with the temperature at which it is preserved. The higher the temperature the more rapid the change. It should be noted further that our results do not seem to accord with those of Gernez. The amount of slowly changing sulphur formed in any particular specimen seems to be proportional to the initial temperature to which the sulphur is heated. Indeed in all of our work we have never obtained any evidence whatsoever that it reaches a maximum at 170°. In fact all specimens of sulphur which were poured at temperatures below 200° were found to change too rapidly to be measured by the methods here employed. It is also a matter of common experience that specimens of plastic sulphur, prepared by pouring boiling sulphur into cold water, crystallize much more slowly than those prepared at lower temperatures.

Effect of the Medium on the Crystallization of Plastic Sulphur.

In our earlier work with Mr. Bassett we got the impression that certain solvents exercise an accelerating influence on the crystallization of plastic sulphur. In order to throw more light on the subject the following experiments were carried out. A specimen of plastic sulphur was divided into several portions. One of these was kept under dilute ammonium hydroxide, a second under 95 per cent alcohol, a third under dilute bromine water, and a fourth under N/10 iodine solution. For the sake of comparison, another portion of the same specimen was kept under water for the desired intervals. The specific gravities of these several specimens were determined at the end of certain intervals, in the usual manner, with the following results:

In Water.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.7925	1.934	0
" " " 1 hour later	0.793	1.935	0.8
" " " 2 hours "	0.7983	1.947	10.8
" " " 3 " "	0.8095	1.972	31.6
" " " 4 " "	0.8225	2.005	59.1
" " " 5 " "	0.832	2.029	79.1
" " " 6 " "	0.8363	2.039	87.5
" " " 7 " "	0.8383	2.04	88.3
" " " 23 " "	0.842	2.054	100.0
" " air	1.6405		

In Dilute Ammonium Hydroxide.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.8545	1.944	0
" " " 1 hour later	0.8595	1.955	12.2
" " " 2 hours "	0.872	1.982	42.2
" " " 3 " "	0.8858	2.013	76.6
" " " 4 " "	0.8952	2.034	100.0
" " air	1.7595		

In Alcohol.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.6567	1.949	0
" " " 1 hour later	0.6567	1.949	0
" " " 2 hours "	0.666	1.977	24.5
" " " 3 " "	0.6805	2.019	61.4
" " " 4 " "	0.69	2.048	86.8
" " " 5 " "	0.6943	2.061	98.2
" " " 6 " "	0.695	2.063	100.0
" " air	1.3482		

In Bromine Water.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.5588	1.936	0
" " " 1.5 hours later	0.575	1.99	36.4
" " " 3 " "	0.5752	1.991	37.1
" " " 8 " "	0.5957	2.064	86.4
" " " 23 " "	0.6012	2.084	100.0
" " air	1.1555		

In N/10 Iodine Solution.

	Grams.	Specific gravity.	Per cent changed.
Weight in water when poured	0.6442	1.908	0
" " " 2 hours later	0.645	1.911	2.1
" " " 3 " "	0.6458	1.913	3.7
" " " 8 " "	0.652	1.93	16.4
" " " 23 " "	0.668	1.975	50.0
" " " 27 " "	0.669	1.978	52.2
" " " 28 " "	0.6807	2.012	77.6
" " " 32 " "	0.6835	2.02	84.3
" " " 43 " "	0.6905	2.042	100.0
" " air	1.353		

It will be observed that ammonia, alcohol, and bromine accelerate the crystallization of plastic sulphur. On the other hand, iodine retards the crystallization to a very marked degree. The last result is in harmony with an observation by Dietzenbacher,[1] who found that by adding 1/400 of its weight of iodine to molten sulphur at 180°, or even lower, a variety of sulphur was obtained which remained plastic for a very long period and which was entirely insoluble in carbon bisulphide.

Plastic Sulphur Has No Definite Melting-point.

All that is known concerning plastic sulphur seems to indicate that it is a supercooled liquid containing one, or probably several, molecular species of the element. It seemed desirable, therefore, to study more closely the effect of heat on the substance with the view of determining whether or not it has a definite melting-point. In order to determine this some fine strands of plastic sulphur were obtained by pouring sulphur, that had been heated to boiling, into cold water. A short cylindrical piece of this was introduced into a melting-point tube and heated gradually in a sulphuric acid bath. At 60° the sulphur was observed to take on a peculiar, dull, roughened appearance. At 90° it became perfectly clear and transparent, and at 109° it began to flow down the walls of the tube. At 114° it was entirely liquid, although considerably darker than molten sulphur that had been prepared by melting the crystalline variety of the element at this temperature. Another specimen of the same plastic sulphur was placed in a melting-point tube and plunged into boiling water. At the end of ten minutes it began to flow, and shortly thereafter changed suddenly to the crystalline variety. It has also been observed that when a quantity of plastic sulphur is suspended by means of a silk thread in boiling water, it begins to flow and soon separates from the thread and drops to the bottom of the vessel. We see, therefore, that plastic sulphur passes into the perfectly liquid form through insensible gradations of temperature; in other words, as is to be expected, it possesses no definite melting-point, the effect of any increase of temperature being simply to diminish its viscosity and to increase its tendency to pass to the crystalline forms of the element.

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[1] Compt. rend., **56**, 39 (1863).

In this connection a very interesting result was obtained. A cylindrical piece of plastic sulphur that had been prepared by pouring boiling sulphur into cold water was placed in a small test-tube. The bottom of the tube was then gently heated in such a manner as to melt the lower end of the sulphur throughout about one-fourth of its length, taking the precaution to preserve the continuity of the fused and unmelted portions. On removing the source of heat, that portion of the sulphur that had been melted, crystallized almost immediately, whereas the unmelted portion remained plastic and perfectly transparent for several hours.

Color Changes in Plastic Sulphur Brought About by Heat.

It is well known that the development of the plastic condition in sulphur is accompanied by marked changes in color, and just as the plasticity persists for a time after cooling, so also the reddish-brown tints resulting from the application of heat are preserved in the specimen for some time after cooling. The one change is always the concomitant of the other, and both are doubtless the outward signs of the same molecular change in liquid sulphur. It is an easy matter to predict the stability of any particular specimen of plastic sulphur from the color alone. As a rule, light, amber-colored specimens of plastic sulphur crystallize easily, whereas reddish-brown varieties remain plastic for longer periods.

Such being the case, it occurred to us that it would not be without interest to study the changes in color of plastic sulphur brought about by heat. In order to do this two melting-point tubes were attached to the same thermometer. In one of these was placed a short cylindrical piece of plastic sulphur, which had been prepared by pouring boiling sulphur into cold water, and which was clear and transparent, and of a reddish-brown color. A few small crystals of orthorhombic sulphur were placed in the second tube, and the thermometer with the tubes attached was placed in a bath of pure sulphuric acid, and the whole gradually heated over a small flame. At 60° the specimen of plastic sulphur became dull and cloudy in appearance, at 90° it regained its transparency, at 102° it began to show signs of flowing, and at 115° it was completely liquid. Another effect of the heat was to deepen the color slightly, so that in the liquid state this specimen had about the same color as an equal amount of N/10 iodine solution. The specimen of orthorhombic sulphur began to melt at 115°, and was completely molten at 120°. It gave a light, amber colored liquid, having a slight greenish tint. The difference in the color of the two specimens was certainly very marked. The flame was now removed and the bath allowed to cool slowly. As was to be expected, the liquid resulting from the melting of the orthorhombic sulphur crystallized first at 78°, whereas the melt from the plastic sulphur did not crystallize until 63° was reached. The flame was again placed under the bath and the tubes reheated. The tube which originally contained the plastic sulphur began to show signs of melting at 107° and was completely molten at 110°. The original orthorhombic specimen now began to melt at 114° and was completely fused at 120°. In the liquid condition each specimen assumed very nearly the same tint as before. On gradual cooling, the specimen resulting from the melting of the orthorhombic variety crystallized at 95°, whereas that resulting from the plastic form crystallized at 80°. Heat was reapplied. The plastic specimen melted at from 113° to 115°, the orthorhombic at 116°. As the result of these successive heatings the two specimens were beginning to show an alteration in color. The original plastic specimen was becoming perceptibly lighter in color, whereas the original orthorhombic specimen was beginning to take on a reddish-brown tint. It therefore occurred to us that if the two specimens were heated for a sufficient length of time they would become alike in color. Accordingly, the two tubes were heated for about five hours at 120° to 125°. At the end of this time both specimens were reddish-brown in color and were practically of the same tint. It is evident, therefore, that whether we start with plastic or orthorhombic sulphur, a chemical equilibrium is ultimately reached as the result of the application of heat to the system.

On the Effect of Tension on the Crystallization of Plastic Sulphur.

It is a matter of common observation that stretching or handling plastic sulphur has a tendency to accelerate its crystallization. This is doubtless the result both of the action of heat and mechanical disturbance. It seemed of interest, therefore, to determine the effect of tension on the crystallization of the substance. Several experiments having this for their object were carried out in this laboratory by Mr. Bassett several years ago. Strands of plastic sulphur of about equal length, were cut from the same piece, and pieces of thin rubber were tied to the ends of the pieces of plastic sulphur. In one case the rubber ends were drawn taut over upright pins, inserted in a block of wood in such a way as to exert considerable tension on the strand of plastic sulphur with which they were connected, whereas the rubber end-pieces connecting the second strand of sulphur were left free and hence exercised no tension on the second strand of plastic sulphur. Both pieces were kept under water during the interval of the experiment. After the lapse of several hours the two pieces of sulphur were removed from the water and disconnected from the rubber strands. They were then dried and weighed, and the amount of soluble sulphur determined in each by bringing them in contact with carbon bisulphide, and weighing the insoluble residue. The following results were obtained :

Experiment 1.

	Per ceut of soluble sulphur found.
Plastic sulphur poured at 300° :	
Under tension	55.13
Not under tension	31.71

Experiment 2.

	Per cent of soluble sulphur found.
Plastic sulphur poured at 350° :	
Under tension	45.24
Not under tension	21.20

In harmony with these results it was invariably found that the specimens of sulphur under tension became brittle, opaque, and crystalline, whereas the strands not under tension remained plastic and translucent during the interval of the experiment.

An interesting confirmation of these results has recently been obtained. Beautifully transparent strands of plastic sulphur were prepared by carefully pouring sulphur that had been heated to 250° into cold water. The strands had an even thickness of about $\frac{1}{8}$ inch. Two of them were cut into lengths of 2 inches each and clamped at the ends by means of delicate rubber clamps. One of them was drawn out so as to increase the original length by about $\frac{1}{2}$ inch, whereas the other was left free. The former, therefore, was under considerable tension whereas the latter was not. Both were kept side by side under water during the experiment. Both remained perfectly clear and transparent for some time. At the end of one and one-half hours, however, relatively large, well-defined crystals began to develop in the longitudinal axis of the strand under tension, whereas the strand not under tension remained perfectly clear and transparent, showing no crystallization whatsoever. At the end of two hours the crystallization had extended almost throughout the piece under tension, whereas in the specimen not under tension only a few crystals were to be seen. The specific gravities of the two pieces were then determined with the following results :

Initial specific gravity	1.94
Specific gravity specimen, not under tension	1.953
Specific gravity specimen, under tension	1.975

The phenomena here under consideration are doubtless altogether analogous to the changes which take place in metals when the latter are subjected to mechanical stress.

The Dilatometric Method of Measuring the Rate of Change of Plastic into Crystalline Sulphur.

Kopp[1] seems to have been the first to employ the dilatometer in measuring the change of volume of sulphur and various other substances produced by heating and melting. More recently Reicher,[1] working in van 't Hoff's laboratory, has employed this instrument in determining the transition temperature of sulphur, and in studying the change of the orthorhombic into the monoclinic variety. The interesting results obtained by these observers naturally suggested that possibly the dilatometer might be employed advantageously in determining the rate of crystallization of plastic sulphur.

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[1] Ann. Chem. (Liebig), **93**, 129–232 (1855).

Several simple forms of the instrument have been employed. One of these was constructed in the following manner: A 50 cc. pipette was fused off near the lower part of the bulb. The upper tube of the pipette was cut off about 1.5 inches from the bulb. The bulb was then filled with water and the required amount of freshly prepared plastic sulphur introduced. The bulb of the apparatus was connected with a millimeter tube, graduated in millimeters, about 2 feet long, by means of a tightly fitting rubber tube. By pushing the graduated tube into the bulb and carefully drawing it out again the column of water in the graduated tube could be adjusted to any desired height. In order to guard against leakage the rubber connection was carefully wrapped with copper wire, and as a further safeguard, the whole connection was covered over with black rubber tire-tape. The bulb of the apparatus was then immersed in water above the level of the rubber connection and the whole apparatus clamped in a vertical position. The gradual fall in the column of water in the millimeter-tube served to indicate the progress of the change, the height of the column being read off at different intervals. The graduated tube was accurately calibrated by means of mercury. The following are some of the results obtained with this form of apparatus:

Experiment 1.

Plastic sulphur poured at 440°.
Amount of sulphur used, 6.8295 grams.
Initial specific gravity of sulphur, 1.923.

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[2] "Études de Dynamique Chimique," van 't Hoff: Eng. Trans., p. 94-95 (1896).

Specific gravity of sulphur when removed from dilatometer, 2.00.

Cubic capacity of dilatometer-tube per centimeter, 0.01319 cc.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	5.6	0	22.5	0
5	6.7	1.1	22.5	0.014509
5	8.7	1.0	22.5	0.01319
5	9.55	0.85	22.5	0.011211
5	10.15	0.6	22.5	0.007914
5	10.5	0.45	22.5	0.005935
5	10.9	0.4	22.5	0.005276
5	11.1	0.2	22.5	0.002638
5	11.3	0.2	22.5	0.002638
5	11.5	0.2	22.5	0.002638
5	11.7	0.2	22.5	0.002638
5	11.85	0.15	22.5	0.001978
5	12.0	0.15	22.75	0.001978
5	12.15	0.15	22.75	0.001978
5	12.2	0.05	23.0	0.000659
5	12.4	0.2	23.0	0.002638
5	12.45	0.05	23.5	0.000659
230	15.9	3.45	22.5	0.045505

Total contraction, 10.3 cm.

Contraction found by dilatometer, 0.1358 cc.

Contraction calculated from difference in specific gravity, 0.1365 cc.

Experiment 2.

Plastic sulphur poured at 250°.

Amount of sulphur used, 4 grams.

Initial specific gravity of sulphur, 1.931.

Specific gravity of sulphur when removed from dilatometer, 2.059.

Capacity of dilatometer tube, 0.01241 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	6.7	0	21	0
3	7.65	0.95	21	0.01188
5	8.075	0.425	21	0.00527
5	8.4	0.325	21	0.00403
5	8.7	0.3	21	0.00372
5	8.95	0.25	21	0.00310
5	9.2	0.25	21	0.00310
5	9.45	0.25	21	0.00310
15	10.05	0.6	21	0.00744
15	10.6	0.55	21	0.00682
15	11.05	0.45	21	0.00568
15	11.45	0.4	21	0.00496
15	11.07	0.25	21	0.00310
945	17.05	5.35	21	0.06649

Total contraction, 10.35 cm.

Contraction found by dilatometer, 0.1284 cc.

Contraction calculated from difference in specific gravity, 0.1288 cc.

A comparison of the readings obtained in the first and second experiments of this series brings out, in a very striking way, the most essential difference between plastic sulphur prepared by pouring sulphur that has been heated only to moderately high temperatures, and that which has been prepared by pouring at temperatures in the vicinity of its boiling-point. A large part of the former always crystallizes almost immediately, whereas in the latter crystallization always proceeds with extreme slowness. The results obtained with the dilatometer therefore simply tend to confirm those of common experience.

With the form of dilatometer first employed, considerable difficulty was experienced on account of the narrow opening of the bulb of the instrument, and the difficulty of introducing the plastic sulphur with sufficient rapidity to avoid crystallization, after the determination of its initial specific gravity. With the view of overcoming this difficulty, recourse was had to the simple form of dilatometer proposed by Kopp.[1] As made by us, the bulb of the instrument consisted of a wide-mouthed homeopathic vial, of about 1 ounce capacity. This was connected to the graduated millimeter-tube by means of a soft perforated cork, which had previously been boiled in oil, in order to render it impervious to water. The wide mouth of the bottle enabled us to introduce the sulphur into the apparatus with great rapidity, so that no time was lost in setting up the apparatus. The height of the column of water in the dilatometer-tube was adjusted to the desired level by alternately pushing in and withdrawing the tube. During the experiment the bulb of the apparatus was immersed in oil above the level of the cork. The following are the results of some experiments that were carried out by means of this instrument:

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[1] See drawing: Ann. Chem. (Liebig), 93, Fig. II. at end of volume.

Experiment 3.

Plastic sulphur poured at 250°.

Amount of sulphur used, 14.6800 grams.

Initial specific gravity of sulphur, 1.901.

Specific gravity of sulphur when removed from dilatometer, 1.941.

Capacity of dilatometer-tube, 0.01319 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	1.2	0	20	0
5	2.5	1.3	20	0.017147
5	3.8	1.3	20	0.017147
5	5.0	1.2	20	0.015828
5	5.8	0.8	20	0.010452
5	6.45	0.65	20	0.008573
5	7.0	0.55	20	0.007254
6.5	7.4	0.4	20	0.005276
5	7.75	0.35	20	0.004616
5	8.0	0.25	20	0.003295
5	8.3	0.3	20	0.003957
5	8.525	0.225	20	0.0029677
5	8.75	0.225	20	0.002967
5	8.975	0.225	20	0.002967
5	9.175	0.2	20	0.002638
5	9.375	0.2	20	0.002638

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
5	9.575	0.2	20	0.002638
5	9.75	0.175	20	0.002308
5	9.95	0.2	20	0.002638
5	10.15	0.2	20.25	0.002638
5	10.45	0.3	20.25	0.003957
5	10.55	0.1	20.25	0.001319
5	10.775	0.225	20.25	0.002967
5	11.15	0.375	20.25	0.004946
5	11.325	0.175	20.25	0.002308
5	11.5	0.175	20.5	0.002308
5	11.7	0.2	20.5	0.002638
5	11.875	0.175	20.5	0.002308
5	12.05	0.175	20.5	0.002308
5	12.2	0.15	20.5	0.001978
5	12.45	0.25	20.5	0.001648
5	12.525	0.075	20.5	0.000989
5	12.7	0.175	20.5	0.002308
5	12.825	0.125	20.5	0.001648
5	12.975	0.15	20.5	0.001978
5	13.1	0.125	20.5	0.001648
17	13.5	0.4	20.5	0.005276

Total contraction, 12.3 cm.

Contraction found by dilatometer, 0.16225 cc.

Contraction calculated from difference in specific gravity, 0.16001 cc.

Experiment 4.

Plastic sulphur poured at 230°.

Amount of sulphur used, 8.4420 grams.

Initial specific gravity of sulphur, 1.911.

Specific gravity of sulphur when removed from dilatometer, 1.972.

Capacity of dilatometer tube, 0.01412 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	2.4	0	20	0
5	4.4	2.0	20	0.02824
5	5.45	1.05	20	0.014826
5	6.05	0.6	20	0.008472
5	6.5	0.45	20	0.006354

Dilatometer Readings (*Continued*).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
5	6.875	0.375	20	0.005295
5	7.175	0.3	20	0.004236
10	7.625	0.45	20	0.006354
5	7.825	0.2	20	0.002824
5	7.975	0.15	20	0.002118
25	8.575	0.6	20	0.008472
15	8.875	0.3	20	0.004236
5	8.925	0.05	20	0.000706
5	9.00	0.075	20	0.001059
11	9.15	0.15	20	0.002118
9	9.3	0.15	20	0.002118
35	9.85	0.55	20	0.00713
100	11.3	1.45	20	0.020474
15	11.5	0.2	20	0.002824
105	12.6	1.1	20	0.015532

Total contraction, 10.2 cm.

Contraction found by dilatometer, 0.1440 cc.

Contraction calculated from difference in specific gravity, 0.1365 cc.

Experiment 5.

Plastic sulphur poured at 220°.

Amount of sulphur used, 20.6900 grams.

Initial specific gravity of sulphur, 1.884.

Specific gravity of sulphur when removed from dilatometer, 1.934.

Capacity of dilatometer tube, 0.01412 cc. per cm.

Dilatometer Readings.

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
0	1.0	0	20	0
1	1.6	0.6	20	0.008472
1	2.15	0.5	20	0.007060
1	2.45	0.3	20	0.004236
1	3.0	0.55	20	0.007766
1	3.55	0.55	20	0.007766
1	4.05	0.5	20	0.007060
1	5.025	0.475	20	0.006707
1	5.5	0.475	19.75	0.006707
1	5.925	0.425	19.75	0.006001

Dilatometer Readings (Continued).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
1	6.375	0.45	19.75	0.006154
1	6.725	0.35	19.75	0.004942
1	7.15	0.425	19.75	0.006001
1	7.525	0.375	19.75	0.005295
1	7.875	0.35	19.75	0.004942
1	8.25	0.375	19.75	0.005295
1	8.625	0.375	19.75	0.005295
1	8.925	0.3	19.75	0.004236
1	9.25	0.325	19.75	0.004588
1	9.505	0.255	19.75	0.0036
1	9.875	0.37	19.75	0.005224
1	10.15	0.275	19.75	0.003883
1	10.4	0.25	19.75	0.00353
1	10.65	0.15	19.75	0.002118
1	10.95	0.3	19.75	0.004236
1	11.2	0.25	19.75	0.003530
1	11.4	0.2	20	0.002824
1	11.65	0.25	20	0.00353
1	11.85	0.2	20	0.002824
1	12.05	0.2	20	0.002824
1	12.275	0.225	20	0.003177
1	12.45	0.175	20	0.002477
1	12.65	0.2	20	0.002824
1	12.825	0.175	20	0.002471
1	13.0	0.175	20	0.002471
1	13.2	0.2	20	0.002824
1	13.35	0.15	20	0.002118
1	13.6	0.25	20	0.003530
1	13.675	0.075	20	0.001059
1	13.8	0.125	20	0.001765
1	13.95	0.15	20	0.002118
1	14.1	0.15	20	0.002118
1	14.25	0.15	20	0.001765
1	14.375	0.125	20	0.001765
1	14.0	0.125	20	0.001765
1	14.62	0.12	20	0.001694
1	14.75	0.13	20	0.001835
1	14.875	0.125	20	0.001765
1	15.0	0.125	20	0.001765
1	15.1	0.1	20	0.001412
1	15.225	0.125	20	0.001765
1	15.325	0.1	20	0.001412

Dilatometer Readings (*Continued*).

Time. Minutes.	Readings.	Increments of contraction.	Temperature.	Contraction in cc.
1	15.425	0.1	20	0.001412
1	15.525	0.1	20	0.001412
1	15.625	0.1	20	0.001412
1	15.7	0.075	20	0.001059
1	15.8	0.1	20	0.001412
1	15.9	0.1	20	0.001412
1	16.0	0.1	20	0.001412
1	16.075	0.075	20	0.001059
3	16.5	0.25	20	0.00353
5	16.85	0.35	20	0.004942
5	17.225	0.275	20	0.003883
5	17.55	0.325	20	0.004588
5	17.85	0.3	20	0.004236
5	18.15	0.3	20	0.004236
5	18.4	0.25	20	0.00353
5	18.65	0.25	20	0.00353
5	18.9	0.25	20	0.00353
5	19.15	0.25	20	0.00353
5	19.4	0.25	20	0.00353
5	19.265	0.225	20	0.003177
5	19.825	0.2	20	0.002824
5	20.025	0.2	20	0.002824
5	20.225	0.2	20	0.002824
5	20.425	0.2	20	0.002824
5	20.6	0.175	20	0.002471
5	20.775	0.175	20	0.002471
5	20.95	0.175	20	0.002471

Total contraction, 19.95 cm.

Contraction found by dilatometer, 0.2815 cc.

Contraction calculated from difference in specific gravity, 0.2834 cc.

For successive intervals of five minutes the contractions show a gradual decrease. On the supposition that the change under consideration is a monomolecular process we have the following values for the coefficient of velocity :

Time. Minutes.	Contractions. cm.	Per cent of change.	*k*.
5	2.55	17.7	0.030288
10	2.375	24.6	0.029781
15	1.95	34.4	0.029103
20	1.63	42.6	0.028492
25	1.445	49.8	0.028190
30	1.10	55.3	0.027350

It will be seen from these numbers that there is a falling off in the velocity of the change, amounting to about 10 per cent, in thirty minutes. This gradual diminution in the rate of crystallization of plastic sulphur is in harmony with the conception that in this supercooled liquid we have to deal not with one, but probably with several molecular species, some of which pass to the crystalline variety of the element more rapidly than others. We have seen that such a conception derives support from various other properties of the substance such as the color, solubility in carbon bisulphide, etc.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, June, 1904.

PERCHROMIC ACID AND THE PERCHROMATES.[1]

BY HORACE G. BYERS[2] AND E. EMMET REID.[3]

HISTORICAL.

The well-known blue compound, formed when solutions of chromic acid or acidified chromates are treated with hydrogen peroxide, was discovered by Barreswill[4] in 1847 and is in common use as a means of detection of both chromic acid and hydrogen peroxide because of the intense blue color of its solution in ether, in which it is comparatively stable. The discoverer assigned to this compound the formula Cr_2O_7, because of the volume of oxygen evolved by it when reacting with hydrogen peroxide. He was unable to obtain any stable compounds of alkalies with it, nor was he able to isolate the substance giving rise to the blue color.

Fairly,[5] by similar means, deduced the formula CrO_6 for the blue substance.

Moissan[6] obtained the blue compound from the ethereal solution by rapid evaporation at —20° as an oily liquid, and showed that in this condition it evolved hydrogen by action on sodium amalgam. From the amount of oxygen which the blue solution evolved by its spontaneous decomposition in the presence of alkalies, he concluded that the blue substance has the composition $CrO_3.H_2O_2$. He states that by its action on the alkali metals chromates are produced.

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[1] This work was begun at the University of Washington and continued, jointly, at the University of Chicago, in the laboratory of General and Physical Chemistry.

[2] University of Washington.

[3] Baylor University, Texas.

[4] Ann. chim. phys., [3], **20**, 2641.

[5] Chem. News, **33**, 237.

[6] Compt. rend., **97**, 96.

Berthelot,[1] studying the compound from the point of view of the oxygen evolved when acidified bichromates are treated with hydrogen peroxide, assigns to the blue compound the probable formula $H.CrO_4.H_2O_2$.

Pechard,[2] by treatment of the aqueous solution of the blue compound with barium hydroxide, obtained a compound to which he assigns the formula $BaCrO_5$.

Hausserman,[3] by treatment of chromium hydroxide with sodium peroxide, obtained a compound to which he assigns the formula $Na_6Cr_2O_{15}.28–30H_2O$.

Wiede[4] prepared from the blue ethereal solution a salt to which he gave the composition $(NH_3)_3CrO_4$, and a series of salts of the organic bases to which he assigns the general formula $RCrO_5$. He also prepared the salts of ammonium, sodium, and potassium, and assigns to these the composition expressed by the formula $MCrO_5H_2O_2$. He concludes, therefore, that the blue solution contains chromium in the state of oxidation implied by the formula Cr_2O_9.

Patten,[5] by reason of the color produced when the blue aqueous solution is treated with a solution of sodium acetate, and because of a purple precipitate formed when the ethereal solution is treated with solid sodium acetate, concludes that the blue solution contains chromium in the state of oxidation conforming to the oxide CrO.

A study of the foregoing literature convinced the authors of the present paper that more work on this subject is desirable, and that the many attempts to get compounds of the blue substance by direct treatment with the alkali metals failed only by reason of the temperature at which these attempts were made. The following investigation resulted :

Compt. rend., **108**, 25 ; **157**, 477.

[2] *Ibid.*, **113**, 39.

[3] J. prakt. Chem., **48**, 70.

[4] Ber. d. chem. Ges., **30**, 2178 ; **31**, 516, 3139 ; **32**, 378.

[5] This JOURNAL, **29**, 385 (1903).

EXPERIMENTAL.

The Potassium Salt.—Acting on the hypothesis that the formation of chromates by the action of alkalies and the alkali metals is due to the decomposition of the product first formed, the blue solution was prepared, using an acidified bichromate solution saturated at the ordinary temperature of the room, and just sufficient 2.5 per cent hydrogen peroxide to give the supernatant layer of ether an intense blue color. This blue solution was cooled to about —20° and freshly cut pieces of potassium dropped in. The low temperature was maintained by the use of solid carbon dioxide, which was placed in an ether-bath surrounding the blue solution or was dropped directly into the latter. A vigorous evolution of gas, which was proved by analysis to be hydrogen, followed the addition of the potassium. At the same time there was produced a purplish-black precipitate, and the blue solution was ultimately decolorized. This precipitate quickly decomposes, when exposed to the air at the room temperature, with the evolution of oxygen and the formation of a substance which proved to be the bichromate. It dissolves in water with the formation of a sherry wine color, and, if the water is ice-cold, only slowly fades to the color of the chromate. It regenerates the blue color when acidified in the presence of ether.

As the compound seems to begin to decompose even below zero the analysis by the usual methods is difficult. Since the compound evolves oxygen on decomposition and forms a dichromate, it was thought that the determination of the available oxygen would be a means of arriving at the composition.

A N/10 solution of potassium bichromate was titrated against a neutral solution of ferrous ammonium sulphate of similar concentration. Measured quantities of the latter, usually 50 cc., were diluted with about 100 cc. of recently boiled water. In the earlier experiments ordinary distilled water was used. Into the iron solution, portions of the potassium salt were dropped, and the solution vigorously stirred. The portions used were washed with cold ether, and care was taken to insure a large excess of iron. The solution was acidified with sulphuric acid and the excess of iron determined by titration against the bichromate solution, using ferricyanide as an indicator.

The titrated solution was then made alkaline with ammonia, boiled, and filtered. The precipitated hydroxides of iron and chromium were dried and fused in an iron crucible with an excess of sodium peroxide and a small piece of potassium hydroxide over a Bunsen burner. The fused mass was dissolved in water, saturated with carbon dioxide, and filtered. The residue was again fused and redissolved. The two solutions were titrated against the iron solution. These titrations give, in the first instance, the oxidizing power of the potassium salt, and in the second, the oxidizing power of its chromium in the known form of the chromate. Of course, deduction was made for the amount of chromium introduced in the first titration.

The following results were obtained, the oxidizing power being expressed in terms of cubic centimeters of N/10 bichromate. The ratio given in the tables is based on the following considerations: In the iron solution, when acidified, the chromates are reduced to the state of oxidation represented by the oxide Cr_2O_3. In the case of the chromate this is represented by $2CrO_3 \rightarrow Cr_2O_3 + 3O$. If the state of oxidation of the chromium in the blue compound corresponds to the oxide Cr_2O_7 the relation would be:

$$Cr_2O_7 \rightarrow Cr_2O_3 + 4O.$$

The ratio of the available oxygen would then be 4 : 3.

Table I.

	Salt solution. cc.	Chromate solution. cc.	Ratio.
1	50.5	39.5	3.84 : 3
2	27.4	19.4	4.24 : 3
3	27.4	19.9	4.14 : 3
4	34.1	25.4	4.03 : 3
5	29.5	21.75	4.07 : 3
		Mean,	4.065

A solution of potassium hydroxide in ether will also precipitate the potassium salt, and determination of the potassium chromate ratio was made upon two samples of the partially dried salt so prepared, with the following results. The potassium was weighed as the sulphate and the chromium as the oxide :

Table II.

	Salt. mg.	Potassium.	Chromium.	Ratio of K : Cr.
1	122	24.6	34.4	1 : 1.38
2	127	27.3	37.7	1 : 1.39
		Calculated ratio,		1 : 1.33

Wiede[1] prepared, in the same way, a salt very similar in appearance to the one under investigation and ascribed to it the formula $KCrO_5.H_2O_2$. He also prepared his salt by precipitation of the blue solution with an alcoholic solution of potassium cyanide. In this salt he continually found the ratio of potassium to chromium as expressed above, but the oxygen values were higher than those obtained by us. He prepared his blue solution by use of a very large excess of hydrogen peroxide, 250 cc. of a 10 per cent solution with 10 grams of chromic anhydride.

It seemed probable that the difference in results is in some way connected with this excess of hydrogen peroxide. To test this point Wiede's salt was prepared, and instead of using his method of analysis the oxidizing power of the salt was determined as previously outlined. The result is given in Table III. The blue solution was then prepared without excess of hydrogen peroxide, and the additional precaution was taken of washing the solution twice with a chromic acid solution. The results in this case are given in Table IV.

Table III.

	Salt.	Chromate.	Ratio.
1	35.0	22.9	4.58 : 3
2	26.5	17.4	4.57 : 3
3	17.3	11.4	4.56 : 3
A second sample :			
1	37.3	24.10	4.66 : 3
2	35.15	22.11	4.77 : 3
3	29.85	19.9	4.49 : 3

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[1] *Loc. cit.*

Table IV.

	Salt.	Chromate.	Ratio.
1	16.9	12.8	3.96 : 3
2	11.1	8.14	3.96 : 3
3	16.2	12.12	3.98 : 3

It seems possible that the large amounts of oxygen indicated in Table III. are due to cryoscopic hydrogen peroxide or to the formation of a compound of another series (see summary at close of article). An attempt was made to obtain a complete analysis of the potassium salt by the following method. Portions of the same sample of the potassium salt used in the analyses given in Table IV. were dropped into tubes, the lower, closed ends of which were surrounded with solid carbon dioxide. The upper ends were then sealed with a blast-lamp. Thus enclosed, the substance changes quietly into the bichromate. On opening these tubes, after weighing, considerable gas escaped and the odor of ether was plainly noticeable. Tubes 1 and 2 (see Table V.) were opened by breaking off the capillary tips by means of an iron rod passing through the stopper of a U-tube in which they were successively placed. The U-tube was immersed in a boiling salt solution and the water from the tubes driven over into weighed calcium chloride tubes by means of carbon dioxide. In tubes 3 and 4 the moisture was determined by weighing the tubes after opening and again after heating to 140° in an air-bath. The contents of each tube were washed into a platinum dish and titrated with the iron solution, the chromium and iron precipitated, and the potassium determined as the sulphate. The chromium precipitate was fused and determined as usual. The results follow. The excess of potassium in 1 and 2 over that required for the bichromate is probably due to potassium cyanide or to potassium carbonate contained in the cyanide used.

Table V.

	I.	II.	III.	IV.
Total substance	70.5	57.9	....	49.17
Weight of gas	9.19	10.9	....	11.6
Weight of moisture	4.11	2.9	4.3	2.4
Weight of solid contents	56.5	44.1	55.3	35.7
Weight of bichromate (by titration)	52.9	40.5	53.18	33.19
Weight of bichromate (by fusion)	52.7	41.2	53.8	34.1
Potassium found	17.1	14.3	14.1	8.84
Calculated potassium (from bichromate found)	14.1	10.7	14.3	8.89

The above results make it clear that the substance yields pure potassium bichromate on spontaneous decomposition, and that the potassium and chromium are present in the same ratio as in the dichromate.

The Sodium Salt.—In the attempt to prepare the sodium salt in the same way as the potassium the difficulty was encountered that the compound which formed was closely adherent to the sodium, and was with difficulty separated from it. Particles of sodium caused trouble when the mass was put into the iron solution. The sodium salt thus prepared is similar in appearance to the potassium salt, but appears to decompose more easily, and at temperatures approaching zero assumes a pasty form. Analysis number 1, given in Table VI., is from the salt thus prepared.

It seemed probable that the substance prepared by Patten[1] is this sodium salt. With this in view the blue ethereal solution was prepared, cooled to —20°, and treated with powdered sodium acetate. A purple precipitate was formed mixed with the excess of acetate. The supernatant ether was found to contain acetic acid. It was shown by blank tests that the excess of acetate interfered in no way with our method of analysis. After decanting the ether and washing thoroughly with cold ether until the residue was free from the blue color, samples were analyzed with results appended :

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[1] *Loc. cit.*

Table VI.

	Salt.	Chromate.	Ratio.
1	23.5	18.2	3.87 : 3
2	32.0	24.10	4.10 : 3
3	30.0	22.5	4.0 : 3
4	47.8	34.5	4.16 : 3
		Mean,	4.01 : 3

The Ammonium Salt.—An ammonium salt was prepared by passing gaseous ammonia into the blue ethereal solution cooled to about —40°. It is probably not necessary to work at such a low temperature, though one attempt to prepare the salt at —10° was without result. The salt is a brownish-yellow, and on analysis gave the results listed in Table VII. No attempt has yet been made to determine its relation to the salt prepared by Wiede and assigned the formula $(NH_3)_3CrO_4$:

Table VII.

	Salt.	Chromate.	Ratio.
1	31.5	23.0	4.11 : 3
2	32.7	23.7	4.14 : 3
3	33.3	24.12	4.13 : 3
		Mean,	4.13 : 3

Other Salts.—By using the acetates of lithium, magnesium, calcium, barium and zinc in the same way as in the case of the sodium, the corresponding salts of these metals were prepared. The magnesium and zinc salts acted only slowly upon the blue solution. All these compounds formed a chocolate-brown slurry with the excess of acetate and the ether used in washing. The analyses were carried out as in the other cases, except that in the case of the barium salt a solution of ferrous chloride was used as a reducing agent, and the solution was acidified with hydrochloric acid. All these compounds decomposed at the room temperature with the evolution of gas and the formation of yellow chromates. Table VIII. contains the results of the analyses :

Table VIII.

	Lithium salt.	Chromate.	Ratio.
1	10.7	8.1	3.98 : 3
2	17.4	12.7	4.10 : 3
		Mean,	4.04 : 3
	Magnesium salt.	Chromate.	Ratio.
1	17.2	13.1	3.94 : 3
	Calcium salt.	Chromate.	Ratio.
1	27.4	19.5	4.12 : 3
2	25.3	19.5	3.94 : 3
3	36.5	27.5	3.98 : 3
4	36.5	28.1	3.83 : 3
		Mean,	3.97 : 3
	Barium salt.	Chromate.	Ratio.
1	24.1	18.1	3.98 : 3
2	25.3	19.25	3.94 : 3
		Mean,	3.96 : 3
	Zinc salt.	Chromate.	Ratio.
1	9.0	6.5	4.15 : 3
2	10.0	7.4	4.05 : 3
		Mean,	4.10 : 3

The average ratio of the oxidizing power of all the salts to that of their chromium in the form of the chromate is 4.02 : 3.

These results point so clearly to the existence in the blue solution of an acid of the composition expressed by the formula $HCrO_4$ (or more probably $H_2Cr_2O_8$), that it was of interest to study the decomposition of the blue compound in the presence of alkalies.

The blue solution, prepared as in the previous experiments, was divided into four 50-cc. portions. One of these was evaporated to dryness in a platinum dish and the residue ignited and weighed as chromium oxide. The second and third were each placed in 250 cc. of recently boiled ice-cold water containing 50 cc. of the standard iron solution and shaken vigorously in a separatory funnel and the oxidizing power determined.

It was found that the ether interfered somewhat with the titration, by reason of surface phenomena, and hence a slight excess of the bichromate was added, and the solution boiled and cooled before completing the titration. The chromium was precipitated, fused, and redetermined as before. The fourth portion was placed in a Lunge nitrometer (capacity 150 cc.) with 60 cc. of dilute caustic soda, confined over mercury. After decomposition was complete the oxygen was determined by absorption in pyrogallol, after removal of the ether vapor. The alkaline solution was titrated against ferrous iron. Since several observers have shown, and as our own experience also shows, that there is a slight reduction below the bichromate stage of oxidation under these conditions, the chromium was reprecipitated and again determined after fusion. The results are given in Table IX.

Table IX.

1 Cr_2O_3 found 0.0738 gram, equivalent to 29.10 cc. N/10 bichromate.

	Blue solution.	Chromate.	Ratio.
2	40.1	30.4	3.96 : 3
3	39.6	29.166	4.01 : 3

4 Volume of oxygen (corr.) 6.5 cc., equivalent to 11.61 cc. N/10 bichromate.

The alkaline solution was found equivalent in oxidizing power to 27.5 cc. bichromate and after fusion to 29.54 cc.

From the literature it appears that most of those who have worked upon this solution have used a large excess of hydrogen peroxide over that needed to effect the state of oxidation here indicated. It was then of interest to see if the presence of a known excess of hydrogen peroxide would affect the nature of the blue solution.

The solution was prepared as before and afterward shaken with an excess of 2.5 per cent hydrogen peroxide The aqueous layer was separated, but the ether portion was not dehydrated. Portions of this solution were then analyzed as before. Fifty cc. of it contained 0.0682 gram of chromic oxide corresponding to 26.88 cc. N/10 bichromate. A second portion of 50 cc., decomposed in the nitrometer as before, gave 10.05 cc. oxygen, equivalent to 17.96 cc. bichromate, while the re-fusion of the precipitated chromate showed itself equivalent to 22.1 cc. Hence the ratio of the oxidizing power of the blue solution to its equivalent chromate is as 5.44 : 3. A 50 cc. portion of the solution, titrated directly against the iron in the former manner, gave as the oxidizing power 62.9 cc., and in the form of the chromate a value of 29.3 cc.—a ratio of 6.4 : 3.

Attention is again called to the fact that this solution was not dehydrated, as that fact has perhaps a bearing on the question referred to in paragraph 3 of the summary.

Summary and Conclusions.

1. The experimental portion of this paper shows conclusively the existence of the perchromates and that they have the general formula $MCrO_4$, or $M_2Cr_2O_8$. The latter formula is perhaps more probable by reason of the analogous persulphates.

2. The blue solution, prepared without excess of hydrogen peroxide, contains the acid corresponding to these salts, *i. e.*, $H_2Cr_2O_8$.

3. The results obtained by Moissan, Pechard, and by us when using a solution prepared with an excess of hydrogen peroxide all point to the probable existence of another compound possessing higher oxidizing capacity. Whether this be true or not is a problem for which it is our hope to find the solution.

We are continuing this work and hope to be able to prepare other salts of this acid and to ascertain the relation of the acid and its salts to the other possible acids of chromium and its allied elements.

OBITUARY.

ALEXANDER WILLIAM WILLIAMSON.

The death of Professor Williamson, LL.D., F.R.S., on May 6th, removes one of the few remaining chemists on whose work the modern ideas of the science are based. Williamson was born May 1, 1824, and had, therefore, just completed his eightieth year. After private preparation, he studied at the Universities of Heidelberg and Giessen, under Gmelin and Liebig, and afterwards for three years in Paris, working at the higher mathematics. In 1849 he was appointed Professor of Practical Chemistry at University College, London, with which institution he remained connected until his retirement, in 1887. Williamson's name will always be known in the history of chemistry on account of his work on etherification, 1850–1854. He showed quite clearly, and for the first time, the true relationship of the alcohols, ethers, and allied bodies to water, and formulated them on the "water type." This, and the subsequent proof afforded by Hofmann, that the amines belong to the "ammonia type" paved the way for the more general conceptions of valency. Williamson was also the first to suggest that there is a continuous process of interchange going on among the atoms composing the molecules of compounds.

CORNELIS ADRIAAN LOBRY DE BRUYN.

C. A. Lobry de Bruyn was born January 1, 1857, at Leenwarden, and died July 23rd, aged forty-seven years. Lobry de Bruyn studied at the University of Leiden, where he was assistant to Franchimont, and subsequently in Paris, under Würtz. In 1885 he was appointed chemist in the Dutch Marine Service, and in 1896 succeeded Gunning as professor at the University of Amsterdam. The work of Lobry de Bruyn which has attracted most attention is probably his isolation of free hydroxylamine in 1891, and of hydrazine in 1894. Both preparations depend on the use of methyl alcohol as solvent, and he studied its action on a number of other substances. A considerable portion of his activity was given to the investigation of the dinitrobenzenes, and he devoted much time to a study of the action of ammonia and dilute alkalies on the sugars. Good work was also done by him in analytical chemistry, and, during the later years of his life, he applied himself with increasing intensity to the solution of problems of general physical chemistry. He was elected a "Foreign Member" of the Chemical Society of London in the earlier part of the present year.

REVIEWS.

Die Chemie der Zuckerarten. Von Prof. Dr. Edmund O. von Lippmann, Direktor der Zuckerraffinerie Halle zu Halle a. S. Dritte völlig umgearbeitete Auflage. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904.

The third edition of this comprehensive work brings the record of investigations up to February, 1904. It comprises in two "half" volumes 1912 pages of text, 39 pages of names of authors cited, and 50 pages of subject-index. The work is dedicated to the memory of Victor Meyer, the early teacher and later friend of the author.

The compilation of such a voluminous work requires an amount of labor almost appalling, which the author has indicated by a quotation from the "Carmina burana" of the thirteenth century:

> "Et ut opus faciant
> Quod non possit mori,
> Moriuntur studio,
> Subditi labori."

Happily, however, for the good of science this stupendous work has not exhausted his activities.

This book contains in compact form, logically arranged, practically everything that is known concerning the chemistry of the sugars. The author has also given all the relations of the sugars of a chemical, physical, and physiological character, as well as their significance for technology, agricultural chemistry, and food chemistry. The greatest possible brevity, consistent with exactness, completeness, and clearness of arrangement characterizes the work throughout.

In the logical arrangement of the work, the monosaccharides are the first treated, and the first "half" volume, of 1034 pages, is given up entirely to their study.

The second "half" volume treats of the sugars which are of the most economic and technical importance. Naturally, the chapter on sucrose or cane-sugar is the one which will attract the greatest attention in industrial quarters. This chapter comprises 388 pages.

Among the disaccharides maltose occupies the most prominent position, and 64 pages are given to the subject.

The trisaccharides occupy 50 pages and raffinose, naturally, is the most important of them from the point of view of applied chemistry.

The tetrasaccharides comprise, at the present time, only two, of which the more important is stachyose.

From the purely chemical standpoint, the fifth subdivision of the work is the most interesting. It treats of the construction, configuration, and synthesis of the sugars. In this division the remarkable work of the past few years in the synthesis of carbohydrates is intelligently set forth.

After the foregoing description of the character of the work it hardly need be said that this is a volume which no chemist interested in physiological or nutrition investigations can well do without. Those interested in theoretical study will also find the work of unusual significance, inasmuch as it sets forth the various theories which have been proposed in regard to the construction and relation of sugars in a clear and satisfactory manner.

A mere glance at the contents of the work shows, more than any words can, the immense strides which have been made in chemical investigations of this character in the past quarter of a century.

It is evident that the only method possible to keep chemists informed of the progress of their science is in the devoted work of specialists in bringing into comprehensive form all that is known of the subject under study.

If the chemistry of the sugars, arranged in the briefest possible statement of our knowledge, forms a volume of 2000 pages it is evident that, in its advance, the science of chemistry has outstripped the possibility of being known by any one human mind.

The author himself regrets the incompleteness of his work and the possibility of errors which may be therein contained. It was impossible to repeat even a small part of the experiments described by others, and in accepting the statements of their work and its conclusions he realizes that many inaccuracies may have crept into the book. This fault is fully recognized in the quotation he makes from LaRochefoucauld:

"Pour bien savoir les choses il en faut savoir le detail; et comme il est presque infini, nos connaissances sont toujours superficielles et imparfaites." H. W. W.

ANALYSE DES MATIÈRES ALIMENTARIES ET RECHERCHE DE LEURS FALSIFICATIONS. Par M. CH. GIRARD, Director du Laboratoire Municipal de Paris. Deuxième Édition Très Augmentée. Paris: Vve. Ch. Dunod, Éditeur. 1904. (Compiled under the direction of M. Chas. Girard by his assistants in the Municipal Laboratory.)

This is a volume of 849 pages devoted to the analysis of food-stuffs and methods of determining their adulterations. This work is largely the result of the experience of M. Chas. Girard, the director of the Municipal Laboratory of Paris.

A recognition of the food value of potable waters is found in the first part of the book, and 80 pages are devoted to that subject. The examinations described are bacteriological and chemical, giving in condensed form the methods of procedure in both cases. An interesting matter connected with the study of waters is the municipal ordinance in regard to the manufacture of ice for consumption. The first article of this ordinance forbids the manufacturer or storekeeper to sell, or place on sale for alimentary purposes, ice which does not give, by melting, potable water, that is, water fit for drinking both from the standpoint of the bacteria which it contains and its chemical composition.

The chapter on wines is naturally one of the most important in the book. It extends from page 81 to 205, inclusive, and is written by M. Sanglé Ferrière. In this chapter the mean composition of the leading varieties of French and foreign wines is given. The red wines of the Gironde, which is the most important of the wine-producing provinces, contain a mean percentage of alcohol, by volume, of 9.6. The white wines of the same class have a mean content of alcohol by volume of 10.1 per cent. The various forms of adulteration of wines are described. They consist chiefly in the adding of sugar to the musts deficient in saccharine matter, and in the mixing of wines made from pomace, to which sugar has also been added, with genuine wines. The different methods of treating wine are defined in full. Of special interest in this connection is the employment of fumes of sulphur to aid in the conservation of wine and in the clearing of white wines. The process of stopping the fermentation in wines is technically called "mutage," and the substances which are most employed in this process are sulphurous acid, alcohol, and salicylic acid. It is stated that the sulphurous acid used is obtained by burning sulphur matches, by the addition of alkaline bisulphites, or by the use of an aqueous solution of sulphurous acid. The Consulting Committee of Hygiene of France has condemned the practice of using salicylic acid in the above process, but condones this of sulphurous acid. Just why that distinction has been made does not appear clear from a hygienic point of view.

The article on the analysis of wines is written by M. Truchon and is an excellent summary of the processes now in use, many of which were devised or improved in the Municipal Laboratory.

The article on beer, extending from page 207 to 242, inclusive, is written by M. J. de Brevans. The definition of purity is as follows: "Beer is an alcoholic drink obtained by the fermentation of infusions or decoctions of germinated barley flavored with hops." This definition excludes from the class of pure beer those varieties made by the fermentation of other cereal grains or of brewing sugars.

The chapter on cider is written by M. Sanglé Ferrière, and extends from page 243 to 262, inclusive. This article is of especial interest on account of the importance of the cider industry in Normandy and other parts of France. The article on vinegar extends from page 263 to 278, inclusive, and is also written by M. Sanglé Ferrière. Vinegar is defined as a product of the acetic fermentation of wine, or of any other alcoholic liquor. The word "vinegar," used in its strictly etymologic sense, can only be regarded as a product of the acetous fermentation of wine. Vinegar made from other sources, therefore, should be named to define their origin, namely, cider vinegar, malt vinegar, spirit vinegar, etc. Methods describing the technical and the analytical processes are complete and satisfactory.

The article on alcohol and spirits extends from page 279 to 352, inclusive, and is written by M. A. Saglier. The article opens with a brief historical sketch and afterwards a description of the different kinds of spirits in common use in France. Naturally, the most important of these beverages is brandy. The methods for the determination of the higher alcohols and the ethereal and aldehydic bodies derived therefrom during the aging of the brandy, are of particular value, and especially useful in this country in determining the purity of imported articles of this class.

The article on milk extends from page 353 to 399, inclusive; that on butter from page 401 to 438, inclusive; and the one on cheese from page 439 to 448, inclusive; all are by M. Ladan Bockairy. It is a remarkable fact that the quick commercial method of determining butter-fat in milk, devised by Babcock, which is entirely satisfactory for all ordinary purposes, is not even mentioned in this chapter.

Shorter articles on edible oils, lard, tallow, meats, cereals, fruits, coffee, tea, cocoa, chocolate, sugars, syrups, confections, preserves, spices, and coloring-matters are given on the same general plan as mentioned above. The analytical and technical discussions are quite full on all of these subjects, and in the main the methods of analysis described are those of most modern use and commonly employed in this country. In many cases, however, many changes in analytical methods, improvements, and even new methods developed in the Municipal Laboratory are given in full. It is these parts of the analytical descriptions which will be found of most value to American readers.

The final chapter on the composition of playthings and the danger of poisoning the children therefrom, is written by M. Girard himself.

The work can be highly commended as of great value to all chemists engaged in the study of foods and the detection of adulterants therein, and in the execution of food laws.

H. W. W.

DIE RIECHSTOFFE. Von DR. GEORG COHN in Görlitz (Zugleich als VI Band, 2 Gruppe. II. Abtheilung von *Bolley-Englers* Handbuch der chemischen Technologie). Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904. 220 pp. Price, 6 marks.

The meaning of the word "Riechstoff" is given by the author as follows: "Ich nenne Riechstoffe natürlich vorkommende oder künstlich gewonnene, bei gewöhnlicher Temperatur flüchtige, chemisch einheitliche Körper, die vermöge ihres Geruches einer Anwendung im Haushalte des Menschen fähig sind. Riechstoffe im engeren Sinne sollen ausserdem die Eigenschaft haben, für den gebildeten normalen Menschen wohlriechend zu sein."

Nitrobenzene, discovered by Mitscherlich in 1834, is the first artificially prepared substance that came into use for the purpose of perfumery. Collas introduced it into commerce under the name "essence of mirbane," and in 1847 Mansfield prepared it by nitrating the benzene from coal-tar. About the year 1850 the esters of organic acids appeared on the English market as apple-oil, pear-oil, etc. In 1844 Cahours showed that methyl salicylate is the chief constituent of the oil of wintergreen. In 1868 Cahours discovered the preparation of benzoic aldehyde from benzal chloride. In 1875 coumarin was obtained synthetically by Perkin, and vanillin by Haarmann, and in 1888 "artificial musk" by Baur.

This book is of interest to the chemist, as it contains much valuable information and is suggestive. It deals with the literature of the subject, its history, the occurrence of the "Riechstoffe" in Nature, their preparation, their physical properties, their chemical conduct, and relations between odor and chemical constitution, the quantitative estimation of the "Riechstoffe," their physiological conduct, and their uses.

The author is of the opinion that the use of odoriferous substances will keep pace with the development of the industry, as has been the case with artificial dyes. "Perhaps," he says, "the maiden of the future will consider whether she shall wear her ionone or her geraniol gown." It is to be hoped that she will not consider artificial or natural musk as desirable under any circumstances. I. R.

A COMPENDIUM OF CHEMISTRY, including General, Inorganic, and Organic Chemistry. By DR. CARL ARNOLD, Professor of Chemistry in the Royal Veterinary School of Hanover. Authorized translation from the eleventh enlarged and revised German edition by JOHN A. MANDEL, SC.D., Professor of Chemistry, Physics, and Physiological Chemistry in the University and Bellevue Hospital Medical College. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904.

It is to be expected that a book which has gone through eleven German editions will be worth translating into English. A great many useful facts and a large amount of chemical information are crowded into its pages, so that it may well serve as a convenient handbook for students and others who are unable to obtain larger works. In the opinion of the reviewer, it excels in this respect rather than as a text-book. It is evident that a book of less than 600 pages, which covers the ground of general, inorganic, and organic chemistry must be greatly condensed, and can devote but little space to the fundamental theories and generalizations of chemistry, and still less to the hundreds of substances mentioned. There are no descriptions of experiments, though under each element are given the principal tests for it.

The book is undoubtedly reliable in statement, and it contains an excellent index. C. E. W.

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A STUDY OF THE CONDUCTIVITIES OF CERTAIN ELECTROLYTES IN WATER, METHYL AND ETHYL ALCOHOLS, AND MIXTURES OF THESE SOLVENTS—RELATION BETWEEN CONDUCTIVITY AND VISCOSITY.

BY HARRY C. JONES AND CHARLES G. CARROLL.

INTRODUCTION AND HISTORICAL REVIEW.

Prior to the proposal of the theory of electrolytic dissociation by Arrhenius, a number of investigations were carried out in which the conductivities of non-aqueous solutions were studied. Since the proposal of the theory there has been a still greater number of similar investigations. These are particularly interesting in the light of certain hypotheses as to the cause of the dissociating power of a solvent. To these hypotheses, and to some of the work in non-aqueous solvents, reference will be made in another part of this paper.

Much less has been done on conductivities in *mixtures of solvents*. A brief review of what has been accomplished in this field is given below.

Lenz[1] measured the conductivities of various salts, potassium iodide, bromide, and chloride, sodium chloride, etc., in mixtures of methyl and ethyl alcohols and water.

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[1] Mem. de. l'Acad. de St. Petersbourg, 7, 30 (1881).

He found that in certain cases the relative resistances can be obtained from the equation

$$r = 100\ (1 + bv),$$

where 100 is taken as the resistance of an aqueous solution of the same per cent, v is the volume per cent of alcohol, and b, a constant. The formula holds best for the mixtures of methyl alcohol and water.

Stephan[1] studied the conductivities of dilute solutions of sodium, potassium, and lithium chlorides, and sodium and potassium iodides in mixtures of ethyl alcohol and water. His investigation will be given a more detailed consideration in the second part of this paper.

Kablukoff[2] determined the conductivity of hydrochloric acid in ethyl alcohol containing varying amounts of water.

Arrhenius[3] investigated the changes in the conductivity of aqueous solutions resulting from the addition to them of small quantities (less than 10 per cent by volume) of non-electrolytes, such as methyl or ethyl alcohols, cane-sugar, acetone, etc. He found that the changes could be expressed by the empirical formula,

$$l = l_0\left(1 + \frac{a}{x}\right)^2,$$

where l is the conductivity in water, l_0 that in the mixture, x the volume per cent of added non-electrolyte, and a a constant peculiar to each non-electrolyte. Where two non-electrolytes were added a similar empirical formula was found to hold. The coefficient α differs not only for different non-electrolytes and different electrolytes, but varies also with concentration, and is greatest when dissociation is least.

Arrhenius concludes that the amount of dissociation is not appreciably changed by addition of small quantities of non-electrolytes. This follows from the fact that the alteration in conductivity is independent of the concentration. Further, he found that the velocity of inversion of cane-sugar is not appreciably influenced by addition of small amounts of non-electrolytes.

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[1] Wied. Ann., **17**, 673 (1882).

[2] Ztschr. phys. Chem., **4**, 432 (1889).

[3] *Ibid.*, **9**, 487 (1892).

Holland[1] worked in the same field as did Arrhenius. His results will be referred to again. Strindberg[2] repeated and confirmed some of Arrhenius' (*loc. cit.*) work.

Wakeman[3] measured the conductivities of various electrolytes: Sodium and potassium chlorides, hydrochloric acid, and numerous organic acids, in mixtures of ethyl alcohol and water (containing 10, 20, 30, 40, and 50 per cent of alcohol).

For the cases studied, the equation

$$\frac{\varDelta}{p(100-p)} = \text{const.}$$

was found to hold, where $\varDelta$ is the difference between the conductivity of the electrolyte in water and in the mixture respectively, and p is the per cent of alcohol by volume.

Schall[4] determined the conductivities of picric acid in aqueous alcohol.

Zelinsky and Krapiwin[5] studied the conductivities of sodium and ammonium iodides and bromides in water, methyl alcohol, and a mixture of the two containing 50 per cent of water by weight, for dilutions from $v = 16$ to $v = 1024$.

Here a striking phenomenon was observed. The conductivities in the 50 per cent mixture were found to be decidedly less than the corresponding conductivities in the pure solvents. This minimum is best seen when the results are plotted as curves, with the conductivities as ordinates and the composition of the mixture as abscissae.

Cohen[6] observed the minimum in the case of potassium iodide. He made a study of the conductivity of potassium iodide in mixtures of ethyl alcohol and water (containing 20, 40, 60, 80, and 99 per cent alcohol). The dilutions ranged from $v = 64$ to $v = 2048$. The minimum manifested itself in the 80 per cent mixture from $v = 512$.

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[1] Wied. Ann., **50**, 261 (1893).

[2] Ztschr. phys. Chem., **14**, 161 (1894).

[3] *Ibid.*, **11**, 49 (1893).

[4] *Ibid.*, **14**, 701 (1894).

[5] *Ibid.*, **21**, 35 (1896).

[6] *Ibid.*, **25**, 31 (1898).

From his own observations, and from those of Wakeman (*loc. cit.*), he concludes that the relation

$$\frac{\mu_v H_2O}{\mu_v H_2O.\mathrm{Alc.}} = \text{constant}$$

holds, being independent of both temperature and concentration; that is, the conductivities compared are approaching a limiting value at the same rate, and either the dissociation is the same, in the case compared, or, for mixtures of alcohol and water, conductivity is not a direct measure of dissociation. Cohen is inclined to the latter view.

Walker and Hambly[1] studied the conductivity of diethylammonium hydrochloride in mixtures of water and ethyl alcohol.

Hantzsch[2] made interesting applications of results obtained by studying conductivities in various mixtures.

Tijmstra[3] investigated the conductivities of solutions obtained by the action of mixtures of methyl or ethyl alcohol and water on sodium. In the case of the mixtures of methyl alcohol and water the minimum was observed.

Roth[4] made a careful study of the conductivity of potassium chloride in mixtures of ethyl alcohol and water containing 8 and 20 per cent alcohol by weight. He found that the relation given by Wakeman (*loc. cit.*) holds, but that this was not the case with Cohen's (*loc. cit.*). The quotient

$$\frac{\mu_v H_2O}{\mu_v H_2O.\mathrm{Alc.}}$$

was found to decrease with increasing dilution, and with increase of the amount of alcohol in the mixture. This, Roth thinks, may indicate a decrease in dissociation. The relation given by Arrhenius (*loc. cit.*) was also found to be valid.

The work of Wolf[5] and of Rudorf[6] needs no consideration here.

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[1] J. Chem. Soc., **71**, 61 (1899).

[2] Ztschr. anorg. Chem., **25**, 332 (1900); Ber. d. chem. Ges., **35**, 1001 (1902).

[3] Proc. Kon. Akad. te Amsterdam, 1903, p. 104.

[4] Ztschr. phys. Chem., **42**, 209 (1903).

[5] *Ibid.*, **40**, 222 (1902).

[6] *Ibid.*, **43**, 257 (1903).

Jones and Lindsay[1] extended the work of Zelinsky and Krapiwin, and of Cohen. The solvents used were water, methyl, ethyl, and isopropyl alcohols, and binary mixtures of these liquids. The salts employed were potassium, cadmium and strontium iodides, ammonium bromide, and lithium nitrate. One result of Jones and Lindsay's work was to show that the minimum is more or less general. Jones and Lindsay worked at two temperatures, 0° and 25°, and showed that in some cases, though the minimum does not occur at the higher temperature, it does occur at the lower one. They also showed that the effect of variation of temperature upon the minimum is to shift it toward a mixture containing a larger per cent of alcohol as the temperature rises.

The first part of this work is a continuation of the investigation of Jones and Lindsay.

PART I.

EXPERIMENTAL WORK.

Apparatus.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "manganin." The resistance coils, manufactured by Leeds & Co., were found to be accurate to within 0.04 per cent. The conductivity cells were of the form used by Jones and Lindsay. The constants of these were determined by means of N/50 and N/500 solutions of potassium chloride. Cells used to determine conductivities of the solvent and of highly diluted solutions were treated in the manner recommended by Whetham.[2] The electrodes were first coated with platinum black in the usual manner, and were afterwards heated to a high temperature in the flame of a blast-lamp. It was found, as Whetham states, that the usual coating of platinum black, in spite of careful and long-continued washing, retains traces of salt that subsequently pass slowly into solution. The oxidizing action of the platinum black is also avoided by this treatment. For the purposes mentioned, electrodes of this kind cannot be too highly recommended. The tone-minimum in the telephone is fully as good as with the ordinary type of electrode.

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[1] This JOURNAL, **28**, 329 (1902).

[2] Phil. Trans., **94**, (A), 321 (1900); Ztschr. phys. Chem., **33**, 346 (1900).

The 25° bath was of the usual (Ostwald) form, and the stirrer was driven by a small hot-air motor. The zero bath was of the type used by Jones and Lindsay, consisting of an outer and inner vessel. The inner vessel and the annular space between the two were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel about an equal weight of water was added. By the foregoing means the temperature of a cell immersed in the ice and water of the inner vessel could be kept for any desired period at 0°.02 to 0°.05 C.

The measuring-flasks, pipettes, and burettes were carefully calibrated.

Solvents.

The water used was purified in the following manner: Ordinary distilled water, after addition of potassium dichromate and sulphuric acid, was redistilled. The distillate was again distilled from chromic acid into, and then from, a solution of barium hydroxide. Where the conductivity of the water thus obtained was above 2×10^{-6}, it was redistilled. In many cases the conductivity was much less than this value.

The methyl and ethyl alcohols were the purest commercial preparations obtainable. Each was subjected to the same treatment. The commercial alcohol was dehydrated by standing in contact with freshly burned lime for several weeks. From this it was distilled, and then allowed to stand over dehydrated copper sulphate for a week or more. When required for use, it was distilled from the copper sulphate, small quantities of sodium being added, and precautions were taken to protect the distillate from access of moisture.

The conductivity of the methyl alcohol thus obtained was usually from 1 to 2×10^{-6}. That of the ethyl alcohol was less.

The acetic acid used was obtained from Bender and Hobein, and was designed for cryoscopic work. The amount of water contained in it was determined, as suggested by Rudorff, by observation of its freezing-point. Its conductivity was less than 2×10^{-6}.

Method of Preparing the Solutions.

The mixtures of solvents were prepared as follows: n cc. of alcohol, for example, were diluted to, say, 100 cc. This is designated as a mixture of "n" per cent alcohol.

Calibrated flasks were used for the dilutions and the temperature was kept to within a few tenths of a degree of the temperature of calibration.

In making up the solutions, the exact amount of the salt in question was put into a measuring-flask, and after addition of a portion of the solvent, the substance was dissolved and the flask filled to the mark. Here also the temperature was kept under control.

Usuallythe original solutions were N/16 or N/32. From these others were made by adding the solvent to a measured portion of the solution. Where the quantity to be used would be too small to be measured with reasonable accuracy, one of the intermediate solutions was taken as a starting-point for further dilution.

Conductivity Measurements.

The constants of the cells used were determined or checked at intervals of a few days. For each determination from three to seven or eight different resistances were used. The values given in the tables are, therefore, the mean of severa determinations. Conductivities throughout are molecular conductivities.

Cadmium Iodide.

The cadmium iodide used was a preparation from Kahlbaum, used by Jones and Lindsay in their work.

Jones and Lindsay measured the conductivity of cadmium iodide in water, methyl alcohol, and mixtures at 25° only. The minimum was not observed. It seemed desirable, therefore, to complete the study of the compound.

The cadmium iodide was dried by being allowed to stand in a desiccator over calcium chloride for a week or more. At first the attempt was made to dry it by prolonged heating in an air-bath at 70° to 80°. It was found that when thus treated, the salt assumed a pinkish hue, which immediately gave place to the pinkish-white of the salt in the ordinary condition, when traces of water were added. No mention of this color change can be found in the literature. Though no traces of decomposition could be detected, the other method of drying was chosen. The original solutions were made by direct weighing.

Table I.—Conductivity of Cadmium Iodide in Water at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	31.16	62.86	1.268
32	40.07	81.82	1.670
64	51.93	107.77	2.114
128	63.85	130.24	2.666
256	76.54	155.55	3.160

Table II.—Conductivity of Cadmium Iodide in 25 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	14.57	33.83	0.770
32	17.68	42.10	0.977
64	22.68	55.02	1.294
128	28.59	70.22	1.665
256	35.36	87.31	2.078

Table III.—Conductivity of Cadmium Iodide in 50 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	9.96	20.82	0.434
32	11.23	24.21	0.519
64	14.21	31.25	0.682
128	18.92	41.61	0.908
256	21.58	51.4	1.193

Table IV.—Conductivity of Cadmium Iodide in 75 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	8.94	15.78	0.274
32	9.71	17.08	0.295
64	11.24	20.08	0.354
128	14.37	25.68	0.452
256	18.58	33.52	0.598

Table V.—Conductivity of Cadmium Iodide in 100 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	10.96	13.39	0.097
32	11.55	14.51	0.118
64	12.66	14.83	0.087
128	13.69	16.82	0.124
256	17.62	20.01	0.096

Table VI.—Comparison of Conductivities at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
16	31.16	14.57	9.96	8.94	10.96
32	40.07	17.68	11.23	9.71	11.55
64	51.93	22.68	14.21	11.28	12.66
128	68.53	31.09	18.92	14.37	13.69
256	76.54	35.36	21.58	18.58	17.62

Table VII.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
16	62.86	33.83	20.82	15.78	13.39
32	81.82	42.10	24.21	17.08	14.51
64	104.77	55.02	31.25	20.08	14.83
128	130.24	70.22	41.61	25.68	16.82
256	155.55	87.31	51.40	33.52	20.01

Table VIII.—Conductivity of Cadmium Iodide in 25 Per Cent Ethyl Alcohol at 25°.

v.	μ_v 25°.
16	26.97
32	34.90
64	44.21
128	54.54
256	69.71

Table IX.—Conductivity of Cadmium Iodide in 50 Per Cent Ethyl Alcohol at 25°.

v.	μ_v 25°.
16	14.03
32	16.19
64	18.93
128	25.66
256	34.89

Table X.—Conductivity of Cadmium Iodide in 75 Per Cent Ethyl Alcohol at 25°.

v.	μ_v 25°.
16	9.43
32	9.52
64	10.94
128	12.27
256	15.16

Table XI.—Conductivity of Cadmium Iodide in 100 Per Cent Ethyl Alcohol at 25°.

v.	μ_v 25°.
16	2.29
32	2.30
64	2.32
128	2.39
256	2.66

Table XII.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C_2H_5OH.
16	62.86	26.97	14.03	9.43	2.29
32	81.82	34.90	16.19	9.52	2.30
64	104.77	44.21	18.93	10.94	2.32
128	130.24	54.54	25.66	12.27	2.39
256	155.55	69.71	34.89	15.16	2.66

From the data given, especially in Tables VI. and VII., it is seen that cadmium iodide does not show the minimum in mixtures of methyl alcohol and water at 25°. At 0°, however, in a 75 per cent mixture, at volumes 16, 32, and 64, the minimum appears. Beyond these dilutions it disappears.

In various mixtures of ethyl alcohol and water at 25° (Table XII.) no minimum appears, although the values observed are in all cases less than would be expected from the rule of averages.

The results are plotted as curves in Figs. I. and II., the ordinates being conductivities, and the abscissas representing the per cent by volume of alcohol.

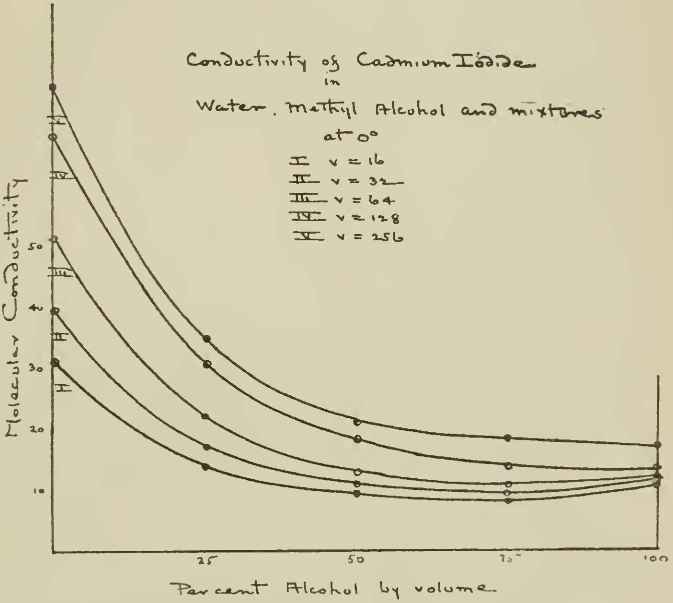

Fig I

Sodium Iodide.

The sodium iodide used was a preparation that had been carefully purified by Jones and Lindsay.

The salt was dried in an air-bath for three days at a temperature of 110° to 130°. This prolonged treatment was found necessary to bring it to constant weight.

The original solutions were made up by direct weighing.

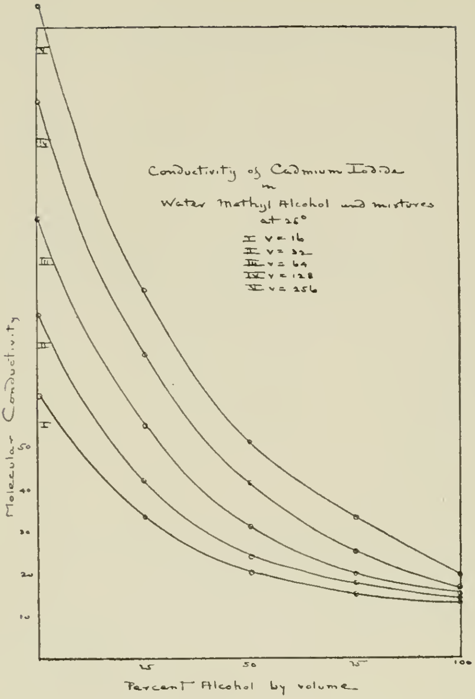

Fig II

Table XIII.—Conductivity of Sodium Iodide in Water at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	μ_v 25°(O).	Temperature coefficient.
32	57.46	106.0	105.7	1.942
64	59.37	109.35	109.3	2.000
128	60.71	112.44	112.3	2.069
256	62.35	115.5	115.2	2.126
512	64.28	118.08	117.9	2.152

The values in the last column are those given by Ostwald.[1] The agreement is seen to be quite satisfactory.

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[1] Ztschr. phys. Chem., 1, 74 (1887).

Table XIV.—Conductivity of Sodium Iodide in 25 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	33.63	70.62	1.48
64	34.68	72.77	1.52
128	35.63	73.78	1.53
256	36.73	74.32	1.504
512	37.83	74.98	1.49

The values at 0° are uncorrected for the conductivity of the solvent.

Table XV.—Conductivity of Sodium Iodide in 50 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	27.91	57.18	1.171
64	28.73	58.30	1.183
128	29.04	59.16	1.205
256	30.32	60.87	1.232
512	32.08	61.62	1.181

Table XVI.—Conductivity of Sodium Iodide in 75 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	31.70	56.50	0.992
64	33.08	59.47	1.056
128	34.16	61.49	1.093
256	34.72	62.74	1.121
512	35.00	63.77	1.151

Table XVII.—Conductivity of Sodium Iodide in 100 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	51.09	72.03	0.838
64	55.95	77.63	0.867
128	58.89	82.70	0.955
256	61.02	86.19	1.009
512	62.56	88.27	1.026

Table XVIII.—Comparison of Conductivities at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	57.46	33.63	27.91	31.70	51.09
64	59.37	34.68	28.73	33.08	55.95
128	60.71	35.63	29.04	34.16	58.89
256	62.35	36.73	30.32	34.72	61.02
512	64.28	37.83	32.08	35.00	62.56

Table XIX.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	106.0	70.62	57.18	56.50	72.03
64	109.35	72.77	58.30	59.47	77.63
128	112.44	73.78	59.16	61.49	82.76
256	115.49	74.33	60.87	62.74	86.19
512	118.08	74.98	61.62	63.77	88.27

From the data given in Tables XVIII. and XIX., and from the curves plotted in the manner already indicated (Fig. III.), it is evident that sodium iodide exhibits the minimum

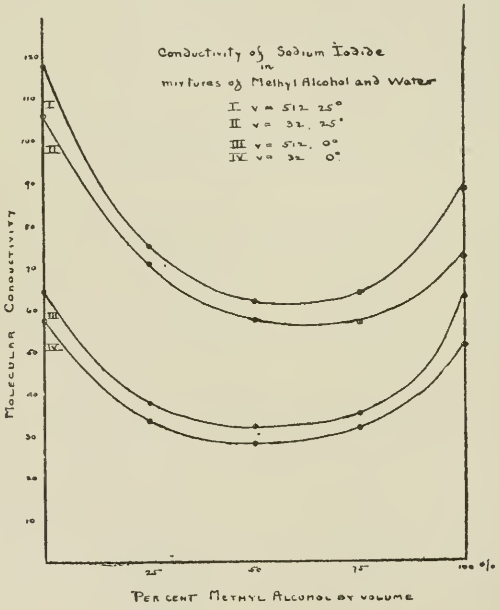

Fig III

in mixtures of methyl alcohol and water. Only two dilutions at the two temperatures of observation have been plotted as the curves would be too close together if all were shown.

The minimum, as Jones and Lindsay have observed, is more pronounced at 0° than at 25°. Further, the shifting effect of change of temperature and of concentration, also observed by Jones and Lindsay, appears at 25°, $v = 32$. The minimum occurs in a 75 per cent mixture; beyond this dilution the minima occur solely in the 50 per cent mixture. At 0° the minimum appears to be exhibited in the 50 per cent mixture alone.

Calcium Nitrate.

It was thought that the study of a ternary salt might prove interesting. Jones and Lindsay had already made a study of strontium iodide, and had found it to exhibit the same phenomena as did binary salts.

The calcium nitrate used was a preparation from Kahlbaum. It was found to be particularly difficult to dehydrate. Heating for several days at a temperature of 130° to 140° was necessary to bring it to constant weight. This treatment caused no perceptible decomposition. All original solutions were made by direct weighing.

Table XX.—Conductivity of Calcium Nitrate in Water at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	94.33	177.56	3.329
32	102.47	189.45	3.440
64	108.35	199.24	3.636
128	113.59	209.93	3.854
256	118.02	215.93	3.916

Table XXI.—Conductivity of Calcium Nitrate in 25 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	53.17	111.45	2.331
32	57.30	120.63	2.533
64	59.81	128.95	2.766
128	63.39	136.81	2.937
256	66.19	141.45	3.010

Table XXII.—Conductivity of Calcium Nitrate in 50 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	41.07	79.04	1.518
32	44.70	90.11	1.816
64	49.15	98.35	1.968
128	53.94	103.68	1.990
256	54.82	109.19	2.175

Table XXIII.—Conductivity of Calcium Nitrate in 75 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	39.59	70.06	1.219
32	43.60	80.16	1.462
64	48.85	89.98	1.645
128	51.90	97.72	1.883
256			

Table XXIV.—Conductivity of Calcium Nitrate in 100 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16		32.79	
32	31.30	41.88	0.423
64	37.27	50.79	0.541
128	46.66	60.52	0.555
256	55.17	73.98	0.752

Table XXV.—Comparison of Conductivities at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
16	94.33	53.17	41.07	39.59	
32	102.47	57.30	44.70	43.60	31.30
64	108.35	59.81	49.15	48.85	37.27
128	113.59	63.39	53.94	51.90	46.66
256	118.02	66.19	54.82		55.17

Table XXVI.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
16	177.56	111.45	79.04	70.06	32.79
32	189.45	120.63	90.11	80.16	41.88
64	199.24	128.95	98.35	89.98	50.79
128	209.93	136.81	103.68	97.72	60.52
256	215.93	141.45	109.19		73.98

Table XXVII.—Conductivity of Calcium Nitrate in 25 Per Cent Ethyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	38.80	92.93	2.065
32	41.84	100.56	2.359
64			
128	48.02	112.93	2.596
256	50.26	119.04	2.750

Table XXVIII.—Conductivity of Calcium Nitrate in 50 Per Cent Ethyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	23.7	60.43	1.469
32	25.89	65.30	1.576
64	27.37	69.83	1.698
128	28.83	74.13	1.812
256	30.30	78.31	1.920

Table XXIX.—Conductivity of Calcium Nitrate in 75 Per Cent Ethyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	19.13	39.08	0.798
32	21.41	44.57	0.926
64			
128	26.71	56.08	1.175
256	28.61	60.79	1.287

Table XXX.—Conductivity of Calcium Nitrate in 100 Per Cent Ethyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	4.89	7.08	0.088
32	7.11	9.57	0.098
64	8.59	12.43	0.153
128	10.74	15.47	0.189
256	12.48	18.57	0.244

Table XXXI.—Comparison of Conductivities at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C_2H_5OH.
16	94.33	38.80	23.7	19.13	4.89
32	102.47	41.84	25.89	21.41	7.11
64	108.35		27.37		8.57
128	113.59	48.02	28.83	26.71	10.74
256	118.02	50.26	30.30	28.61	12.48

Table XXXII.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C_2H_5OH.
16	177.56	92.93	60.43	39.08	7.08
32	189.45	100.56	65.30	44.57	9.57
64	199.24		69.83		12.43
128	207.93	112.93	74.13	56.08	15.47
256	215.93	119.04	78.31	60.79	18.57

From the data given in Tables XXV., XXVI., XXXI., and XXXII., and from inspection of the corresponding curves, it is evident that calcium nitrate in no case exhibits the minimum. The conductivities are always less than the proper average.

The relation found by Wakeman,[1]

$$\frac{\Delta}{p(100-p)} = \text{const.},$$

does not hold in the cases thus far studied; nor does that found by Cohen.[1]

Hydrochloric Acid.

In the study of hydrochloric acid the solutions were made as follows: The solvent was prepared in the usual manner. Into a portion of the solvent, kept cool by ice, dry hydrochloric acid gas was passed. This was obtained by allowing concentrated sulphuric acid to drop slowly from a dropping-funnel into pure, aqueous, hydrochloric acid. The gas was dried by passing through two gas-washing bottles containing concentrated sulphuric acid. The vessel containing the solvent into which the gas was passed was protected from extraneous moisture by a drying-tube containing phosphorus pentoxide.

The strength of the original solution was determined volumetrically by means of a standard solution of ammonium hydroxide, methyl orange being used as the indicator. From this solution the dilutions were made, control determinations being carried out on some of them because only the tolerably dilute ones in mixtures and in pure methyl alcohol were found to be stable.

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[1] *Loc. cit.*

The composition of the 69.75 per cent mixture was determined by means of its specific gravity.

Table XXXIII.—Conductivity of Hydrochloric Acid in 50 Per Cent Methyl Alcohol at 25°.

v.	μ_v 25°.
33.05	172.45
132.21	166.09
264.42	165.30
528.83	155.29

Table XXXIV.—Conductivity of Hydrochloric Acid in 69.75 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.
44.67	63.83	116.0
92.42	67.06	123.77
178.75	66.49	117.8
357.5	64.66	118.1
714.72	66.19	116.87

Table XXXV.—Conductivity of Hydrochloric Acid in 90 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.
31.53	46.59	73.79
63.07	47.60	76.19
157.67	51.84	84.27
252.28	51.84	84.27
252.28	51.85	84.38
504.56		84.22

Table XXXVI.—Conductivity of Hydrochloric Acid in 100 Per Cent Methyl Alcohol at 0° and at 25°.

v.	μ_v 0°.	μ_v 25°.
8.42	67.36	95.83
32.8	77.06	110.50
130.26	79.84	118.79
481.44	89.79	129.87
2104.0	95.46	133.44

A consideration of the results, Tables XXXIII., XXXIV., XXXV., XXXVI., shows that in certain cases they are irregular and unexpected. In the 50 per cent mixture the conductivity falls from the first dilution, which is analogous to what has been observed for hydrochloric acid in ether and isoamyl alcohol by Cattaneo[1] and Kablukoff,[2] and for sulphuric acid in acetic acid by Jones.[3] In all these cases the molecular conductivities decreased with decreasing dilution.

In the 69.75 per cent a maximum is reached at $v = 92.42$ at both 0° and 25°. From this point on the conductivities decrease slightly. However, at 0° the mean of the last four conductivities, including the maximum, differs from the maximum value by only 1.5 per cent.

In the 90 per cent mixture the results are perfectly regular, and, what is surprising, a limiting value is reached at $v = 157.67$.

In methyl alcohol the results are also regular, but there is no indication of a maximum value for conductivity. The values found agree in most cases very we with those of Carrara,[4] whose results are also irregular.

It is seen, further, that hydrochloric acid shows the minimum (Fig. IV.) in both the 69.75 per cent and 90 per cent mixtures. At 25° the minimum appears in the former after the dilution $v = 178.75$. At 0° it appears at all dilutions. Carrara[4] also observed the minimum in the case of hydrochloric acid, finding it to occur in methyl alcohol containing about 2 per cent of water.

The conductivity curves (Fig. IV.) for $v = 33$ are plotted.

Sodium Acetate in Mixtures of Acetic Acid and Water.

Thus far we have been concerned with conductivities in mixtures of alcohol and water. An investigation by Jones and Murray[5] seemed to make it advisable to study conductivities in other mixtures—notably of acetic or formic acid and water. The connection of the two investigations will be considered when we come to discuss the cause of the minimum.

As stated, the acetic acid used was a preparation intended for cryoscopic work. The amount of water in this acid was determined by means of its freezing-point, as recommended by Rüdorff.[1] The substance froze at 15°.47. From the tables given by Rüdorff (*loc. cit.*) it contained in 100 parts by weight 0.6 part by weight of water. Knowing the composition of the acid, the proper amounts to be used in making the mixtures could be calculated.

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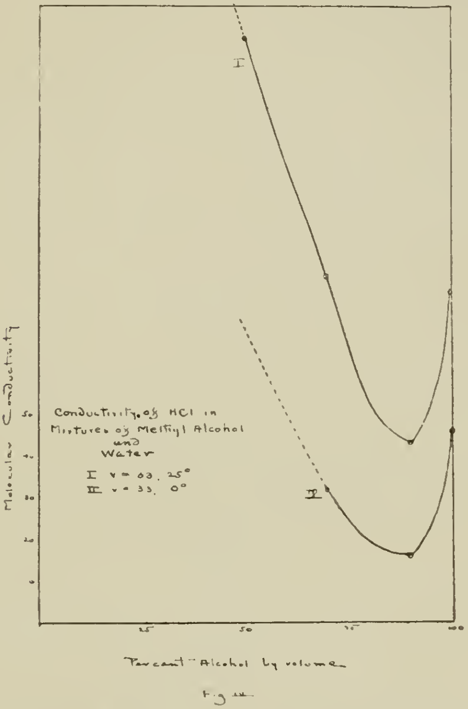
[1] Atti. R. Acc. delle Sc., Torino, **28**, 329; Rend. R. Accad. dei Lincei, (5), **2**, 295.

[2] Ztschr. phys. Chem., **4**, 431 (1889).

[3] This JOURNAL, **16**, 1 (1894).

[4] Gazz. chim. ital., **26**, (1), 119 (1896).

[5] This JOURNAL, **30**, 193 (1903).



The acid was partially frozen and the liquid portion rejected. After melting the solid acid the process was repeated. The specimen thus obtained was used for the conductivities in the pure solvent. Owing to inevitable exposure to the moisture of the air it was not thought profitable to try to remove the last traces of moisture.

In this part of the problem new complications arose, since acetic acid, in aqueous solution, conducts the current.

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[1] Ber. d. chem. Ges., 3, 390 (1870).

The sodium acetate used was a specimen of the fused salt obtained from Kahlbaum. It was dried for two days in an air-bath at 120° to 130°. The original solutions were made up by direct weighing.

The specific conductivity of the solvent (containing 25, 50, 75, and 100 per cent by volume of acetic acid) was determined; then that of the solution in question. The difference between the latter and the former was multiplied by the volume to give the (apparent) molecular conductivity.

Table XXXVII.—Conductivity of Sodium Acetate in 25 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 1.631.

v.	Specific conductivity of solution.	μ_v 25°.
32	2.040	17.89
64	1.469	—10.37

Table XXXVIII.—Conductivity of Sodium Acetate in 50 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 0.8584.

v.	Specific conductivity of solution.	μ_v 25°.
32	1.388	16.84
64	0.9263	4.36
128	0.8986	5.15

Table XXXIX.—Conductivity of Sodium Acetate in 75 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 0.0558.

v.	Specific conductivity of solution.	μ_v 25°.
32	0.7050	20.77
64	0.4446	24.87
128	0.2999	31.24

Table XL.—Conductivity of Sodium Acetate in Acetic Acid at 25°.

Conductivity of solvent = 1×10^{-6}.

v.	Specific conductivity of solution.	μ_v 25°.
32	0.00418	0.134
64	0.00236	0.161
128	0.00129	0.165

On examination, the results are seen to be irregular, and no conclusions can be drawn from them. In the 25 per cent mixture, the molecular conductivity is apparently negative. This, of course, means nothing more than that the specific conductivity of the solvent is greater than that of the solution. Only in the 75 per cent mixture is there any regularity observed. Here the (apparent) molecular conductivities increase with decreasing concentration.

In the pure solvent the conductivities are so small as to be almost negligible. This is not surprising. Wakeman[1] has determined the conductivity of hydrochloric acid in acetic acid, and has found it to be exceedingly small. For example, for $v = 98.56$ μ_v was found to be 1.78.

The irregular results in mixtures of acetic acid and water are to be explained as being due possibly to mutual isohydric influence of dissolved substance and solvent. The dissociation of the sodium acetate is driven back by the presence of the acetic acid, and *vice versa*. This influence is most marked where the dissociation of each separately would be greatest, *i. e.*, in mixtures of lower per cent of acetic acid, and of minimal concentration of sodium acetate.

Since these phenomena have no direct connection with the problem in hand, no further discussion is necessary, especially as the question has been treated by Wolf[2] and by Rüdorff.[2]

PART II.

Dissociation in Fifty Per Cent Methyl Alcohol.

It has been seen that in the case of hydrochloric acid in mixtures of methyl alcohol and water, limiting values for conductivity are reached at a smaller dilution than in either water or methyl alcohol. It is important to see whether this is a general phenomenon.

The limiting values in the case of sodium and potassium iodides and potassium bromide were determined. Throughout this part of the work the utmost care was taken in the preparation of solvents and solutions and in making the dilutions. The cells used were standardized before and after each series of measurements. The conductivity of the solvent was carefully determined and the necessary corrections were made. The water and the methyl alcohol used had a conductivity of not over 1×10^{-6}. All results given are the mean of from five to ten different values.

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[1] Ztschr. phys. Chem., 15, 181 (1894).

[2] *Loc. cit.*

Potassium Iodide.

The potassium iodide was a preparation furnished by Kahlbaum. The flame test showed that no appreciable impurity was present. The salt was dried at 100° to 110° for a day. The values obtained were:

v.	μ_v 25°.
400	69.29
2000	70.58
4000	70.60

The value for the conductivity at $v = 400$ agrees with the (interpolated) value obtained by Zelinsky and Krapiwin,[1] and our results may therefore be incorporated with theirs. This has been done in the following table. The degree of dissociation has been calculated for each dilution. Included in the table, for comparison, are similar values calculated from data obtained by Ostwald[1] for potassium iodide in water, and from data given by Carrara[1] for potassium iodide in methyl alcohol.

Table XLI.—Conductivity of Potassium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol at 25°.

	H_2O.	50 Per cent CH_3OH.	CH_3OH.
v.	μ_v 25°.	μ_v 25°.	μ_v 25°.
16	124.5	62.13	68.14
32	128.5	64.37	74.42
64	130.5	66.01	79.85
128	133.0	67.45	84.70
256	135.8	68.28	88.25
400		69.20	
512	137.9	69.65	90.82
1024	140.9	70.55	93.07
2000		70.58	
4000		70.60	
∞	142.6	70.58	97.63

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[1] *Loc. cit.*

The values of the dissociation factors are shown in the following table. From an inspection of the data it is seen that a limiting value for conductivity is reached at a lower dilution in the mixture than in the other solvents.

Table XLII.—Dissociation of Potassium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol.

	H_2O.	50 Per cent CH_3OH.	CH_3OH.
v.	α.	α.	α.
16	0.873	0.880	0.697
32	0.900	0.912	0.762
64	0.915	0.936	0.818
128	0.931	0.956	0.868
256	0.953	0.968	0.904
512	0.967	0.987	0.931
1024	0.989	1.000	0.954

An inspection of this table shows that, at corresponding dilutions, *dissociation as calculated from conductivity is greater in the mixture than in methyl alcohol or in water.* The only other solvent thus far shown to have a greater dissociation power than water is liquid hydrocyanic acid, as appears from the work of Centnerszwer.[1] Potassium iodide was one of the substances used.

Sodium Iodide.

The sodium iodide was the preparation previously employed. The following measurements were made :

v.	μ_v 25°.
500	60.92
2000	61.72
4000	61.65

Combining these with the values previously obtained by ourselves, and using Carrara's[2] values for conductivities in water and methyl alcohol, respectively, we have the following :

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[1] Ztschr. phys. Chem., **39**, 217 (1902).

[2] *Loc. cit.*

Table XLIII.—Conductivity of Sodium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol at 25°.

	H_2O.	50 Per cent CH_3OH.	CH_3OH.
v.	μ_v 25°.	μ_v 25°.	μ_v 25°.
32	106.0	57.18	68.75
64	109.3	58.30	73.11
128	112.4	59.16	77.31
256	115.5	60.87	79.90
512	118.1	61.27	82.15
2000		61.72	
4000		61.65	
∞	121.4	61.68	89.77

It is evident, in this case, that the results are of the same general character as those found for potassium iodide.

Table XLIV.—Dissociation of Sodium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol.

	H_2O.	50 Per cent CH_3OH.	CH_3OH.
v.	α.	α.	α.
32	0.865	0.927	0.766
64	0.901	0.946	0.816
128	0.917	0.959	0.861
256	0.949	0.987	0.890
512	0.971	0.993	0.915
2000		1.000	
4000	1.000	1.000	

Here also, as was found for potassium iodide, the dissociation is greatest in the mixture.

The following measurements were made for potassium bromide in 50 per cent methyl alcohol:

v.	μ_v 25°.
250	65.78
1250	69.26
2500	69.35

At $v = 250$ the dissociation is 0.949 for the mixture.

At $v = 256$ the dissociation is 0.927 for water, as calculated from Ostwald's[1] and Carrara's[1] values.

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[1] *Loc. cit.*

Table XLV.—Dissociation of Ammonium Bromide in 50 Per Cent Methyl Alcohol.

	50 Per cent CH_3OH.
v.	*α*.
16	0.871
32	0.910
64	0.942
128	0.962
256	0.974
512	0.986
1024	1.000

The values for the dissociation constants are seen to be about the same as those for potassium iodide. Data for conductivity in aqueous solution could not be found. The values for methyl alcohol are calculated from Carrara's data; those for the mixture, from Zelinsky and Krapiwin's.

Table XLVI.—Dissociation of Ammonium Iodide in 50 Per Cent Methyl Alcohol.

	50 Per cent CH_3OH.
v.	*α*.
16	0.875
32	0.909
64	0.943
128	0.967
256	0.973
512	0.994
1024	1.000

Here the values are about the same as for ammonium bromide. No reliable records could be found for ammonium iodide in water. The data for the mixture and for methyl alcohol were furnished by Zelinsky and Krapiwin and by Carrara, respectively.

From results given by Jones and Lindsay it is possible to calculate the dissociation of lithium nitrate in the 50 per cent mixture at two temperatures, 0° and 25°, assuming that here, as in the other cases, complete dissociation is reached at $v = 1024$. It is known that in aqueous solution complete dissociation is not reached as soon in the case of lithium salts as in those of potassium or sodium salts. Less value must therefore be attached to the following results:

Table XLVII.—Dissociation of Lithium Nitrate in 50 Per Cent Methyl Alcohol at 0° and at 25°.

v.	α 0°.	α 25°.
32	0.863	0.862
64	0.899	0.899
128	0.915	0.926
256	0.944	0.964
512	0.963	0.982
1024	1.000	1.000

Values of the dissociation for hydrochloric acid in the 90 per cent and in the 69.75 per cent mixture at 0° and at 25° are also given. It will be remembered that the results in the latter mixture were irregular. No stress can, therefore, be laid upon these figures. We have taken the determinations for $v = 92.4$ as the limiting values in this case.

Table XLVIII.—Dissociation of Hydrochloric Acid in 69.75 Per Cent and 90 Per Cent Methyl Alcohol, in Water and in Methyl Alcohol.

	69.75 Per cent CH_3OH.		90 Per cent CH_3OH.		H_2O.	CH_3OH.	
v.	α 0°.	α 25°.	α 0°.	α 25°.	α 25°.	α 25°.	v
31.5			0.900	0.875	0.909	0.890	37.74
44.67	0.981	0.937				0.916	75.47
63.0			0.919	0.924			
92.42	1.000	1.000				0.972	150.9
158			1.000	1.000			
252			1.000	1.000	0.934		

The values for conductivities in water are taken from Ostwald;[1] those for methyl alcohol from Carrara.[2]

Here it is observed that the dissociation is greater in the 60.75 per cent mixture than in water at the corresponding dilution. This, however, is not the case for the 90 per cent mixture.

It is also interesting to note that apparently in both mixtures the dissociation is greater at 0° than it is at 25°, and the same is true for the 90 per cent mixture, where the results are more reliable than those for the 69.75 per cent mixture.

[1] J. prakt. Chem., **140**, 300 (1885).

[2] *Loc. cit.*

We have suggested that the dissociation in the 50 per cent mixture may be due to the presence of the hydrate $CH_3OH, 3H_2O$. This compound would be more stable at a lower than at a higher temperature, and would be present at the lower temperature to a greater extent, and therefore the dissociation would be greater. This result should be shown by salts as well as by hydrochloric acid, but data are not at hand for comparison. Jones and Lindsay's values for lithium nitrat are available and have been used (Table XL.). From this table, apparently, the dissociation is greater at the higher temperature. But, as we have said, no final conclusions can be drawn from these data, since we cannot be certain that limiting conductivity values were reached by Jones and Lindsay. In the case of hydrochloric acid, however, they were reached, in at least one instance. Further investigation will be needed to decide this matter.

It is interesting at this point to see whether the hypothesis of Dutoit and Aston[1] is quantitatively true for the cases that have been considered. This hypothesis is that the dissociating power of a solvent is dependent upon its association, as determined by the surface-tension method of Ramsay and Shields.[2] If the hypothesis held quantitatively it could be formulated thus:

$$\frac{\alpha}{\alpha'} = \frac{x}{x'},$$

where α and α' are the dissociations of the solutions compared, and x and x' the association factors of the solvents. The relation may be put into the form—

$$\frac{\alpha}{x} = \text{const.}$$

In comparing solutions in different solvents, there should be the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of each solvent. Where solutions in water, methyl alcohol, and ethyl alcohol are to be compared, the dilutions will have the ratio 18, 40, 58 approximately.

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[1] Compt. rend., **125**, 240 (1897).

[2] Ztschr. phys. Chem., **12**, 433 (1893).

We have made a comparison on this basis, for potassium and sodium iodide in water, and methyl and ethyl alcohols. For the ethyl alcohol solution the dissociation was calculated from the data of Völlmer.[1] The others were taken from the preceding tables.

Table XLIX.—$\frac{\alpha}{x}$ *for Potassium and Sodium Iodides in Water and Methyl and Ethyl Alcohols at 25°.*

	H_2O. $x = 3.68$. Constant.	CH_3OH. $x = 3.43$. Constant.	C_2H_5OH. $x = 2.74$. Constant.	
KI	24.9	25.3	24.9	
NaI	23.5	23.7	23.6	$v = 32, 64, 100$
	24.5	25.1		$v = 64, 128$
KBr	25.8	26.2		$v = 128, 256$

Similarly, assuming that Dutoit and Aston's hypothesis holds for 50 per cent methyl alcohol, we may calculate its degree of association. Taking the value of the constant as 23.6, and the comparable volume for the mixture as 48, from the relation $\frac{\alpha}{x} = 23.6$ we can find x. We have $\frac{93.7}{x} = 23.6$, whence $x = 3.96$.

A mixture of methyl alcohol and water, containing 50 per cent methyl alcohol by volume, has very approximately the composition corresponding to the hydrate $CH_3OH,3H_2O$. The existence of alcoholic hydrates has been made probable on other grounds. *It is possible that such hydrates, in virtue of their complexity, have high dissociating power. The greater dissociation found in the 50 per cent mixture may be due to this hydrate, in which four simple molecules combine to form a complex molecule. In water the number of molecules combined at ordinary temperatures is less than four.*

PART III.

Cause of the Minimum.

The first observers of the conductivity minimum, Zelinsky and Krapiwin, offered no satisfactory explanation of it. They suggested that it might be connected with the formation of compounds with methyl alcohol. Further than this they did not go. Jones and Lindsay offered the following explanation: "According to the theory of Dutoit and Aston, it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this be true, it is probable, since those substances which dissociate dissolved electrolytes also show, in general, a normal molecular weight for dissolved non-electrolytes, that this breaking-down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either methyl or ethyl alcohol, or a mixture of methyl alcohol and ethyl alcohol. In these cases, since the molecules of the mixture are less associated than those of the constituents, we should expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which we have worked this is exactly what has been observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

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[1] Wied. Ann., **52**, 328 (1894).

In support of the above view that one associated solvent can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurements. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal, while the surface-tension method of Ramsay and Shields shows, beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the state of aggregation of an associated liquid, it would be expected that at the higher temperature the influence of the solvents on each other would be less than at the lower temperature. That such is the case can be seen by comparing the results at 0° with those at 25°."

The explanation offered by Jones and Lindsay was later strengthened by an investigation by Jones and Murray.[1] They showed, from a study of the freezing-points of solutions of acetic and formic acids, and water—acetic acid in formic acid, formic acid in acetic acid, acetic acid in water, etc.—that the association of one solvent is diminished by the presence of another associated solvent.

According to the explanation offered by Jones and Lindsay, the chief effect producing the minimum is the diminution of dissociation and consequent decrease in conductivity. We have shown that, in the 50 per cent mixture of methyl alcohol and water, the dissociation, instead of being diminished by the presence of the alcohol (or by bringing together water and the alcohol), is actually increased. This fact alone makes it evident that the explanation offered by Jones and Lindsay does not account for the phenomenon.

Two factors determine conductivity—the amount of dissociation and ionic mobility. Decrease in one or both of these produces decrease in conductivity. We have shown that the decrease in conductivity in question cannot be due to decrease in dissociation. The inevitable conclusion is, then, that it is due to a decrease in ionic mobility.

A complete explanation of the minimum in conductivity will have to account for the following facts:

1. The effect itself.

2. The fact that the effect is more pronounced at a lower temperature than at a higher.

3. The fact that rise in temperature (and in some cases increase in concentration) shifts the minimum toward a mixture containing a larger per cent of alcohol.

There is a close connection between the viscosity or fluidity of a solvent and the conductivity of electrolytes when dissolved in the solvent. The greater the fluidity, or the less the viscosity, other things being equal, the greater is the conductivity. This close relationship is shown by the fact that, for certain aqueous solutions, the temperature coefficients of conductivity and of fluidity are identical. The connection between conductivity and fluidity, or viscosity, will be considered in detail in the concluding part of this paper.

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[1] This Journal, 30, 193 (1903).

The investigations of Jones and Lindsay, Zelinsky and Krapiwin, and of ourselves have had to do with conductivities in mixtures of solvents. Numerous researches have been made on the viscosities of mixtures of liquids, notably by Graham,[1] Noack,[2] Pagliani and Battelli,[3] and Traube.[4] All of these workers have found that, in the case of mixtures of various alcohols and water, a striking phenomenon is observed; the viscosity of the mixture is much greater than would be expected from the law of averages. This is best shown graphically by plotting the viscosities as ordinates and the percentage composition of the mixtures as abscissae. The viscosity curve is seen to pass through a maximum. The fluidity of a liquid is the reciprocal of its viscosity. If, therefore, we show graphically the variations in fluidity as the variations in viscosity were shown, the fluidity curve is seen to pass through a minimum. In all cases, of course, the fluidity is less than the average.

The mixtures in which the minimum of conductivity is found to occur are approximately the mixtures in which this minimum of fluidity appears. The explanation of the conductivity minimum that we offer is the following :

The minimum of conductivity is caused primarily by the great decrease of fluidity resulting when the two components of the mixture are brought together.

From the results of Pagliani and Battelli[5] and of Traube[5] we have calculated the various fluidities of mixtures of methyl and ethyl alcohol and water, for the temperatures 0°, 10°, 20°, and 30°, and have plotted the fluidity curves (Figs. V. and VI.) in the manner indicated.

From a consideration of these curves it is evident that, for mixtures of water and methyl alcohol at 0°, the minimum of

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[1] Ann. Chem. (Liebig), **120**, 90 (1861).

[2] Wied. Ann., **27**, 289 (1886).

[3] Atti. di R Ac. delle Sc. d. Torino., **20**, 607 (1885).

[4] Ber. d. chem. Ges., **19**, 871 (1889).

[5] *Loc. cit.*

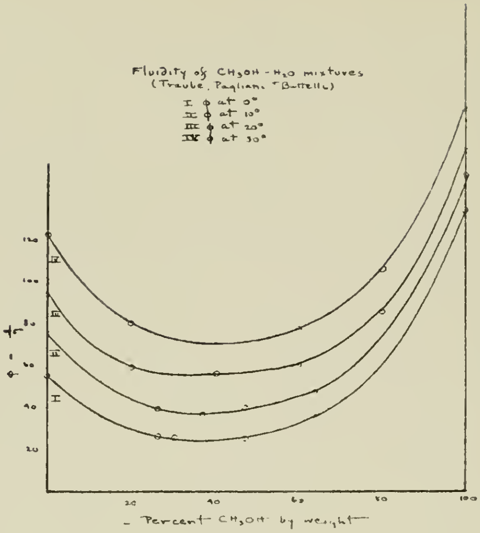

Fig V

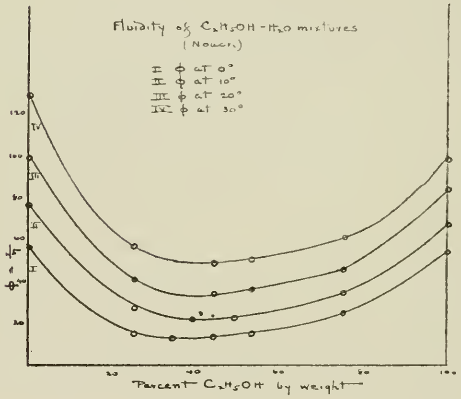

Fig VI

fluidity occurs in a mixture containing 31 per cent methyl alcohol by weight (37 per cent by volume); at 20° the minimum occurs in a 40 per cent mixture (46 per cent by volume). Further, the drop in fluidity is more pronounced the lower the temperature.

For the mixtures of ethyl alcohol and water, at 0°, the minimum occurs in a 34 per cent (40 per cent by volume) mixture. At 30° it is found in a 50 per cent (56 per cent) mixture. The minimum is also more pronounced at the lower temperature.

It should be noted that the change in fluidity is very small over a considerable range—particularly in the case of mixtures of ethyl alcohol and water. At 30° the change of fluidity between 30 per cent and 60 per cent is very slight.

We have here fulfilled all the requirements of a complete explanation of the minimum. The two phenomena are parallel throughout—they are either casually related or have a common cause. The former supposition is much more probable, particularly in the light of the connection between conductivity and fluidity.

The parallelism may be summed up as follows :

1. The conductivity minimum is found to be accompanied by a minimum in fluidity.

2. Both minima are more pronounced at lower temperatures, and both occur at approximately the same points.

3. The effect of increase in temperature is the same upon both minima—there is a shifting towards a mixture containing a greater per cent of alcohol, but the fluidity minimum, so to speak, lags behind the conductivity minimum.

For comparison, the following tables are taken from the work of Jones and Lindsay :

Table L.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 0°.

v.	0 Per cent.	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent.	100 Per cent CH_3OH.
64	74.09	....	35.48	33.73	35.12	39.03	59.32
128	76.41	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.01	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

Table LI.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 25°.

v.	0 Per cent.	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent.	100 Per cent CH_3OH.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0

It is seen that at 0° the minimum of conductivity occurs in a 50 per cent mixture; the fluidity minimum occurs in a 40 per cent mixture. At 25° the minima occur in 65 per cent and 56 per cent mixtures, respectively.

Strontium iodide also presents a good example of the shifting of the minimum, as the following tables from Jones and Lindsay's work show:

Table LII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	113.1	63.00	50.19	55.53	75.82
64	117.7	66.05	52.61	59.24	85.01
128	122.1	68.62	55.05	62.85	94.76
256	126.0	70.98	57.18	66.68	104.4
512	129.8	73.10	59.51	69.98	114.0
1024	132.6	75.51	61.03	73.22	123.4

Table LIII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.8	152.3	120.1	118.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	245.9	161.9	128.5	131.4	166.3

In the case of strontium iodide the real minimum would probably be found in a mixture between the 50 and 75 per cent mixtures.

So, also, in the case of lithium nitrate, as shown in the following tables taken from the work of Jones and Lindsay :

Table LIV.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of These Solvents at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	50.00	29.15	23.59	26.67	45.97
64	51.49	29.68	24.49	27.95	50.12
128	52.51	30.15	25.03	28.66	53.95
256	53.40	30.70	25.71	29.51	56.67
512	54.70	31.35	26.35	30.64	60.06
1024	55.30	32.56	27.35	31.91	63.40

Table LV.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of These Solvents at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH_3OH.
32	91.83	60.56	47.87	47.06	63.51
64	94.62	62.16	49.92	49.52	69.32
128	98.00	63.77	51.50	51.64	74.51
256	99.68	64.96	53.57	54.36	80.57
512	101.3	66.78	54.62	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

An examination of our own values for sodium iodide (p. 533) shows that at 0° the minimum occurs in the 50 per cent mixture. At 25°, for one dilution, $v = 32$; it occurs in the 75 per cent mixture, elsewhere in the 50 per cent mixture. In all probability the real minimum would be found in an intermediate mixture.

When we attempt a comparison for ethyl alcohol the data are more meager. The minimum was found by Jones and Lindsay to occur only at 0° in the cases studied by them. Their data are given :

Table LVI.—Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of These Solvents at 0°.

	H_2O.	Mixture.	C_2H_5OH.
v.	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	74.22	19.42	16.71
128	75.23	19.89	18.83
256	76.62	20.09	19.66
512	77.49	20.70	22.66
1024	77.78	21.50	22.88

Table LVII.—Comparison of the Molecular Conductivity of Potassium Iodide in Ethyl Alcohol, Water, and a 50 Per Cent Mixture of These Solvents at 0°.

	H_2O.	Mixture.	C_2H_5OH.
v.	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	74.09	19.26	19.12
128	76.4	19.82	21.36
256	77.01	20.35	22.66
512	78.0	20.92	25.00
1024	77.96	21.43	27.43

Table LVIII.—Comparison of the Molecular Conductivities of Lithium Nitrate at 0°.

	H_2O.	50 Per cent mixture.	C_2H_5OH.
v.	μ_v 0°.	μ_v 0°.	μ_v 0°.
32	50.0	13.10	14.29
64	51.49	13.56	15.60
128	52.51	14.27	17.52
256	53.40	14.63	19.39
512	54.70	15.45	21.36
1024	55.30	16.25	23.29

An examination of these data shows that the apparent minimum occurs in a 50 per cent mixture. The fluidity minimum occurs in a 40 per cent mixture. The true conductivity minimum might, however, occur at some other point, and, consequently, it is hardly safe to press the matter too far.

Jones and Lindsay also made some measurements in mixtures of methyl and ethyl alcohols. No minimum was observed, the conductivities found being about what would be expected from the law of averages. This is clearly due to the fact that, when these two solvents are brought together, they do not exhibit the same phenomenon as is shown in the case of mixtures of the alcohols and water. We have not found any satisfactory data relative to the fluidity of mixtures of methyl and ethyl alcohols. Arrhenius[1] states that there is no striking change when the two are brought together.

The best method of comparing the variation in conductivity and in fluidity is not in the discussion of the conductivity and fluidity curves, which can only be approximate, it is better to compare the respective ratios of decrease (by per cent) of the two—that is, the differences in per cent from what would be expected from the rule of averages. These average values may be found graphically as follows: At the extremities of a straight line of chosen length, erect perpendiculars proportional in length to the respective conductivities (or fluidities) in the two components of the mixtures, and connect these by a straight line. Divide the base line into parts proportional to the composition of the various mixtures. The perpendiculars joining these points of division and the line previously drawn will be proportional in length to the various average conductivities (or fluidities). This can best be done by the use of coordinate paper. The foregoing method has been used in making the following comparisons:

Table LIX.—Variation ($\Delta\mu_v$) in Conductivity (Percentage Fall in Conductivity) of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 25°.[2]

	20 Per cent.	40 Per cent.	60 Per cent.	80 Per cent. C_2H_5OH by volume.
v.	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.
128	0.329	0.465	0.443	0.308
256	0.334	0.472	0.450	0.311
512	0.340	0.481	0.463	0.334
1024	0.339	0.483	0.464	0.344
2048	0.340	0.482	0.464	0.343
Variation in fluidity	0.461	0.627	0.601	0.466

It is seen that the variation in fluidity is in all cases greater than the variation in conductivity. The two variations must be compared in order to see where the effect of variation is greatest. If the two effects were exactly equal, $\frac{\varDelta\varphi - \varDelta\mu_v}{\varDelta\varphi}$ would equal zero. In this relation we have a means of comparing the two effects. We have made the comparison in the following table:

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[1] Ztschr. phys. Chem., 1, 287 (1887).

[2] The conductivity data are taken from the work of Cohen (*loc. cit.*).

Table LX.—Comparison of Variations in Conductivity and in Fluidity.

v.	20 Per cent. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.	40 Per cent. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.	60 Per cent. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.	80 Per cent C_2H_5OH by volume. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.
128	0.287	0.258	0.263	0.339
256	0.282	0.247	0.258	0.333
512	0.239	0.231	0.232	0.283
1024	0.239	0.231	0.232	0.262
2048	0.239	0.231	0.232	0.262

It is evident that the effect of variation of fluidity on conductivity is greatest in the 40 per cent mixture, for here the values of the quotients are least. It is seen that the effect increases with increasing dilution, and finally becomes constant.

Similar comparisons are given for potassium iodide in mixtures of methyl alcohol and water at 0° and at 25°, using Jones and Lindsay's results.

Table LXI.—Variation (Percentage Fall) in Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 25° and at 0°.

		20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent CH_3OH by volume.
v.		$\varDelta\mu_v$.	$\varDelta\mu_v$.	$\varDelta\mu_v$.	$\varDelta\mu_v$.	$\varDelta\mu_v$.
64	—0°		0.479	0.494	0.456	
	25°	0.237	0.356	0.372	0.350	0.267
128	—0°	0.361	0.507	0.510	0.478	
	25°	0.257	0.368	0.386	0.360	0.283
256	—0°	0.365	0.509	0.502	0.486	
	25°	0.262	0.377	0.394	0.371	0.300
512	—0°	0.366	0.510	0.513	0.489	
	25°	0.262	0.379	0.399	0.381	0.313
1024	—0°	0.361	0.503	0.508	0.490	
	25°	0.262	0.379	0.402	0.386	0.320
	0°	0.543	0.695	0.695	0.682	
	25°		0.575			

Table LXII.—Comparison of Variation in Fluidity and in Conductivity, $\frac{\Delta\varphi-\Delta\mu_v.}{\Delta\varphi}$.

v.	20 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.	40 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.	50 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.	65 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.	80 Per cent CH_3OH by volume. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.
64 —0°		0.311	0.289	0.331	
25°	0.354	0.309	0.304	0.329	0.385
128 —0°	0.335	0.275	0.266	0.299	
25°	0.300	0.285	0.276	0.321	0.346
256 —0°	0.325	0.268	0.261	0.300	0.309
512 —0°	0.326	0.266	0.262	0.282	
25°	0.289	0.264	0.251	0.281	0.279
1024 —0°	0.335	0.276	0.270	0.282	
25°	0.286	0.264	0.246	0.272	0.262

In the following table comparison is made for lithium nitrate :

Table LXIII.—Variation (Percentage Fall) in Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol aud Water at 0° and 25°. (From Jones and Lindsay's Data.)

v.	25 Per cent. $\Delta\mu_v$.	50 Per cent. Δu_v.	75 Per cent CH_3OH by volume. $\Delta\mu_v$.
32 —0°	0.406	0.508	0.432
25°	0.285	0.384	0.333
64 —0°	0.417	0.518	0.443
25°	0.296	0.392	0.345
128 —0°	0.432	0.532	0.466
25°	0.307	0.403	0.358
256 —0°	0.436	0.535	0.472
25°	0.314	0.406	0.362
512 —0°	0.441	0.541	0.477
25°	0.310	0.408	0.354
1024 —0°	0.434	0.541	0.477
25°	0.300	0.411	0.354
—0°	0.600	0.695	0.661
25°	0.456	0.575	0.481

Table LXIV.—Comparison of Variation in Conductivity and in Fluidity, $\frac{\Delta\varphi - \Delta\mu_v}{\Delta\varphi}$, at 0° and at 25°.

$v.$	25 Per cent. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.	50 Per cent. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.	75 Per cent CH_3OH by volume. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.
32 —0°	0.323	0.269	0.345
25°	0.375	0.332	0.308
64 —0°	0.305	0.255	0.330
25°	0.351	0.318	0.283
128 —0°	0.280	0.235	0.294
25°	0.327	0.300	(0.255)
256 —0°	0.273	0.230	0.284
25°	0.311	0.294	(0.247)
512 —0°	0.265	0.222	0.277
25°	0.318	0.290	0.264
1024 —0°	0.277	0.222	0.277
25°	(0.344)	0.285	0.264

In the following tables are given the data for sodium iodide, using our own results:

Table LXV.—Variation (Percentage Fall) in Conductivity of Sodium Iodide in Mixtures of Methyl Alcohol and Water at 0° and at 25°.

$v.$	25 Per cent. $\Delta\mu_v$.	50 Per cent. $\Delta\mu_v$.	75 Per cent CH_3OH $\Delta\mu_v$.
32 —0°	0.400	0.485	0.411
25°	0.277	0.357	0.298
64 —0°	0.406	0.505	0.419
25°	0.283	0.378	0.310
128 —0°	0.409	0.515	0.423
25°	0.297	0.395	0.318
256 —0°	0.408	0.508	0.433
25°	0.313	0.395	0.330
512 —0°	0.409	0.500	0.446
25°	0.321	0.402	0.333

Table LXVI.—Comparison of Variations in Fluidity and Conductivity.

v.	25 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.	50 Per cent. $\frac{\Delta\phi-\Delta\mu_v}{\phi\Delta}$.	75 Per cent CH_3OH. $\frac{\Delta\phi-\Delta\mu_v}{\Delta\phi}$.
32 —0°	0.333	0.302	0.378
25°	0.392	0.379	0.384
64 —0°	0.323	0.273	0.366
25°	0.379	0.343	0.355
128 —0°	0.320	0.260	0.360
25°	0.348	0.318	0.339
256 —0°	0.320	0.269	0.345
25°	0.313	0.313	0.314
512 —0°	0.320	0.281	0.325
25°	0.296	0.301	0.308

Finally we give a comparison of the temperature coefficients of conductivity for various electrolytes and the temperature coefficients of fluidity for the various mixtures.

The volumes were 1024 for KI, $LiNO_3$, SrI_2; 256 for NaI; 128 for CdI_2.

The temperature coefficients are seen to be most nearly equal in the 65 per cent mixture for potassium iodide; for the other salts in the 50 per cent mixture.

Table LXVII.—Comparison of Temperature Coefficients of Conductivity and Fluidity for Various Electrolytes in Ethyl Alcohol-Water Mixtures.

	0 Per cent.	35 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C_2H_5OH.
φ —0°	55.39	22.8	14.15	25.6	55.5
φ —25°	112.00	60.7	41.77	55.1	85.88
$\frac{1}{\varphi_{25^\circ}} \cdot \frac{\Delta\varphi}{\Delta t}$	0.0249	0.0250	0.0264	0.0216	0.0142
$\frac{1}{\mu_{25^\circ}} \cdot \frac{\Delta\mu}{\Delta t}$					
KI $v = 1024$	0.0172		0.0237		0.0135
$LiNO_3$ $v = 1024$	0.0184		0.0251		0.0138
SrI_2 $v = 1024$	0.0272		0.0247		0.0199
$(Ca(NO_3)_2$	0.0182	0.0233	0.0245	0.0210	0.0131) $v=256$

Table LXVIII.—Comparison of Temperature Coefficients of Conductivity and of Fluidity for Various Electrolytes in Methyl Alcohol-Water Mixtures.

	25 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	75 Per cent.	100 Per cent CH_3OH.
φ —0°	30.6	27.0	27.8	34.5	39.75	131.3 —3°.8
φ —25°	69.04	63.4	60.65	68.9	81.83	182.1 —25°.4
$\frac{1}{\varphi_{25^\circ}} \cdot \frac{\Delta\varphi}{\Delta t}$	0.0223	0.0230	0.0216	0.0200	0.0205	0.0123
$\frac{1}{\mu_{25^\circ}} \cdot \frac{\Delta\mu_v}{\Delta t}$						
KI		0.0205	0.0197	0.0187		0.0121
NaI	0.0202		0.0202		0.0179	0.0117
$LiNO_3$	0.0211		0.0203		0.0182	0.0118
						$v = 256$
SrI_2	0.0213		0.0210		0.0177	0.0104
CdI_2	0.0238		0.0220		0.0178	

The temperature coefficients were calculated from Noack's[1] data.

It is evident from these values that for the four salts KI, $LiNO_3$, SrI_2, and $Ca(NO_3)_2$, the quotient $\frac{\mu_v}{\varphi}$ is constant to within 10 per cent (5 per cent for $LiNO_3$).

For the binary salts, and for calcium nitrate this holds for the pure solvent, ethyl alcohol, even more closely.

Discussion of Results.

The value of the quotient $\frac{\Delta\varphi - \Delta\mu_v}{\Delta\varphi}$ is a measure of the parallelism between the two phenomena, decrease in conductivity and decrease in fluidity. If the decrease was the same in both cases, other conditions being the same, the value of the quotient would be zero. The fact that it is not zero indicates that the decrease in ionic mobility resulting from the decrease in fluidity is not proportional to this latter.

When we come to compare the effect in the case of potassium iodide in mixtures of the two alcohols and water (Tables LV. and LVII.), it is seen that the effect of decrease of fluidity on ionic mobility is greatest in the ethyl alcohol mixtures, or the two effects are here most nearly parallel. The effect is less for potassium iodide in methyl alcohol mixtures at both temperatures of observation, 0° and 25°. It is to be remembered that we are leaving out of account possible differences of dissociation. Increase in dissociation (in the mixture) over that of the corresponding aqueous solution would subtract from the effect of decrease in fluidity. Apparently, this possible change in dissociation cannot be very great, as some of our measurements show—not more than 1 or 2 per cent. A far greater and entirely impossible change in dissociation would be necessary to account for the difference in the two effects.

The "minimum" is much more pronounced in the methyl alcohol mixtures. It occurs, however, in the ethyl alcohol mixtures generally at 0°, but is not very marked. We have just seen that the real effect is greater in the latter case, when we make a proper comparison. The reason why it is not so evident in the case of the ethyl alcohol mixtures is to be found in the small conductivities in ethyl alcohol, these, in turn, as will be shown in the last part of this paper, being small, on account of the relatively great viscosity of ethyl alcohol, and its rather small dissociating power. On the other hand, the phenomenon does exhibit itself in the other mixtures, and this is because of the high conductivities in methyl alcohol, these being high on account of the small viscosity of methyl alcohol and its relatively great dissociating power.

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[1] *Loc. cit.*

Considering all of the salts in the various mixtures, it is seen that, in general, the effect of increased viscosity on conductivity is greatest in that mixture in which the minimum in conductivity occurs. In some cases the maximum effect occurs elsewhere. For example, for lithium nitrate (Table LX.) at 25° the maximum effect is in the 75 per cent mixture, while the minimum in conductivity occurs for the most part in the 50 per cent mixture.

The explanation of this is found in the fact that, although in the one mixture the effect is greater, it is offset by the effect of the smaller fluidity of the other mixture, that of the 75 per cent mixture being 81.8, and that of the 50 per cent mixture being only 68.9. In cases where the minimum shifts with increase in dilution, the probable explanation is to be found in the increase of dissociation accompanying further dilution.

The result of variation in the temperature is also shown in the tables—particularly in the case of the lithium salt (Table LX.). At 0° the maximum effect is in the 50 per cent mixture, at 25° in the 75 per cent mixture.

In the last two tables (LXIII. and LXIV.) is given a comparison of the temperature coefficients of fluidity and of conductivity for various electrolytes in the various mixtures of methyl alcohol and water, and also for ethyl alcohol mixtures, for which the data are more meager.

From Table LXIII. it is evident that the temperature coefficients of conductivity and fluidity do not differ markedly, particularly for some salts. For potassium iodide they are most nearly equal in the 65 per cent mixture, differing by only 7 per cent. For the other salts in the 50 per cent mixture the agreement is closest, and the differences are in no cases greater than for potassium iodide in the 65 per cent mixture. In some instances the agreement is seen to be much closer (SrI_2, CdI_2).

For the ethyl alcohol mixture, 50 per cent, the temperature coefficients differ to about the same degree as in the methyl alcohol mixtures. In other words, $\frac{\mu_v}{\varphi}$ = constant.

These facts are significant, as will appear from the latter part of this paper.

Our conclusion is, then, that the decrease in conductivity of electrolytes in binary mixtures of various alcohols and water, which is in some cases accompanied by the minimum conductivity observed by Zelinsky and Krapiwin, is caused primarily by a diminution in the fluidity of the solvent, and a consequent decrease in ionic mobility.

Viscosity and Conductivity.

The viscosity of a liquid or solution is defined as being the force (in dynes) necessary to move a layer of the liquid or solution 1 molecule in thickness, and of unit area (1 sq. cm.) over another layer of the liquid, with unit velocity (1 cm. per sec.). The symbol η is used for the coefficient of viscosity. The fluidity of a liquid is the reciprocal of its viscosity $= \frac{1}{\eta}$.

Two methods have been used in the determination of viscosity. That of Coulomb, in which the coefficient is calculated from observations on the damping of the oscillation of a solid oscillating in the liquid, and that of Poisenille, which derives the constant from observation on the rate of flow of the liquid through a capillary tube.

That there is a connection between the viscosity of a solvent and the electrical resistance of solutions of electrolytes in the solvent, has long been known. Or, what amounts to the same thing, there is a parallelism between fluidity and conductivity.

There have been a number of investigations bearing on this relation. The earliest is that of Wiedemann.[1] Wiedemann's method of varying the fluidity of the solution was by varying the concentration. From his study of solutions of copper sulphate of different concentrations, Wiedemann concluded that the conductivity is directly proportional to the viscosity of the solution; that is, $\frac{K\eta}{p} = \text{const.}$, where K is the conductivity, η the coefficient of viscosity, and p the concentration of the solution in parts by weight of electrolyte to 100 parts of solvent.

Grotrian,[2] in his investigation, used a second method of varying fluidity, that is, by varying the temperature. A comparison was made between the temperature coefficients of fluidity and of conductivity. Grotrian found that in many cases the two coefficients are approximately the same. Wiedemann and Grotrian had worked with solutions of rather high concentration. Thinking that less irregularities would be exhibited by dilute solutions, Stephan[3] made a study of the conductivities of dilute solutions, containing not more than 5 per cent of sodium, potassium, and lithium chlorides, and of sodium and potassium iodides, in mixtures of ethyl alcohol and water. Stephan thus used the third possible method of varying fluidity—that of varying the solvent. Mixtures of alcohol and water were used because of certain striking phenomena exhibited by them. When alcohol is added to water there is a remarkable increase in viscosity over and above what would be expected from the rule of averages. Shown graphically, by plotting the composition of various mixtures as ordinates and the viscosity of the mixtures as abscissas, the viscosity curve is seen to pass through a maximum. These facts have been illustrated and more fully treated in the first part of this paper. Stephan also studied the effect of temperature upon the conductivities and fluidities involved, and found, as had Grotrian[4] in other cases, that the temperature coefficients of both are approximately equal.

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[1] Pogg. Ann., **99**, 229 (1856).

[2] *Ibid.*, **157**, 130 (1876).

[3] Wied. Ann., **17**, 673 (1883).

[4] *Loc. cit.*

Stephan thought he established the relations

$$k = \frac{\mathrm{KH}}{\eta} \qquad \text{and} \qquad k = \frac{w}{w'} \cdot \frac{\mathrm{KH}}{\eta},$$

the first holding for all mixtures up to the mixture with minimum fluidity, and the second from this point on. K in both formulas is the conductivity of the equivalent solution of the salt, k is its conductivity in the mixture, H and η are the viscosity coefficients for water and for the mixture respectively. In the second relation, w is the per cent of water in the mixture, and w' the per cent of water in the aqueous alcoholic mixture of minimal fluidity. Stephan's conclusion is that ionic friction is either proportional to internal friction or equal to it (viscosity); that each ion carries with it neighboring molecules of the solvent, and that the ionic friction consists in friction between these and the rest of the solvent.

The agreement with these formulas was not very close, particularly in the case of the second. Why this is so can be readily seen. Stephan did not take into account one important factor in conductivity—dissociation. Certainly, with various mixtures, there would be varying degrees of dissociation.

Grossmann[1] made use of the data furnished by Grotrian, whose determinations of viscosity were made by the method of Coulomb. By the aid of a new formula, devised by himself, Grossmann recalculated Grotrian's results, and concluded that the product of the viscosity and the conductivity of a solution is constant, and independent of the temperature. This constancy is shown by the fact that the temperature coefficients of conductivity and of viscosity (as calculated by his method) are the same to within less than 1 per cent, and in most cases to within less than one-half of 1 per cent. This he showed to be true for solutions of the chlorides of potassium, sodium, calcium, and magnesium, and of zinc sulphate. Here the great difficulty is in the method used; its validity would have to be granted, and it is questionable whether this can be done.

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[1] Wied. Ann., 18, 119 (1883).

Arrhenius,[1] in the investigation already referred to, on the effect of the addition of small quantities of non-electrolytes on the conductivity of aqueous solutions, found an empirical relation between the conductivity of the solution and the viscosity of the solvent. The equation is—

$$1000\,a = c + 1000\,c'\,(A - 1),$$

where c and c' are constants for the given solvent, A is the viscosity of a 1 per cent aqueous solution of the non-electrolyte (that of water being taken as unity), and a is the coefficient a in the equation,

$$l = l_0\left(1 + \frac{a}{2x}\right)^2,$$

the meaning of which has already been explained.

Holland[2] worked in the same field as did Arrhenius. He found the relations of Stephan, already cited, inapplicable to the cases studied by him, and also that of Arrhenius just given. Holland concludes that though there is a connection between conductivity and viscosity, it is unknown.

Strindberg[3] merely repeated and confirmed some of the work of Arrhenius.

Völlmer,[4] in an admirable investigation on the conductivities of various salts in methyl and ethyl alcohols, took occasion to determine the temperature coefficients of conductivity of the solutions studied, and found that these differed very little from the temperature coefficients of viscosity of the solvents, particularly for solutions in ethyl alcohol. For example, the temperature coefficient of conductivity—the mean value of $\Delta\mu_v$ for seven salts in ethyl alcohol solution—was 1.84 per cent, $\Delta\eta$ being 1.78 per cent; similarly, the mean value of $\Delta\mu_v$ for six salts in methyl alcohol solution was 1.3 per cent, $\Delta\eta$ for methyl alcohol being 1.45. In every case, at high dilutions, there was found to be a parallelism between the two temperature coefficients.

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[1] Ztschr. phys. Chem., **9**, 487 (1892).

[2] Wied. Ann., **50**, 261 (1892).

[3] Ztschr. phys. Chem., **14**, 221 (1894).

[4] Wied. Ann., **52**, 328 (1892).

Euler,[1] extending the work of Arrhenius[2] on the viscosity of mixtures, finds a connection between viscosity and ionic mobility. Arrhenius had proposed the exponential formula,

$$\text{H}(x,y) = \text{A}^x\text{B}^x \quad \text{or} \quad \eta_x = \text{A}^x,$$

where H is the viscosity of the mixture, A and B are characteristic constants, x the volume per cent of the first component, and y the volume per cent of the second. In the second formula, which is another way of stating the first, A is the viscosity coefficient of a normal solution of the second component in the first as solvent, x the volume per cent. Euler extends the formula to partially dissociated electrolytes in solution, giving it the form :

$$\text{H} = \text{S}^x\text{A}^x\text{K}^x,$$

assigning a part of the viscosity to each component, S being that for the undissociated portion of the electrolyte, A and K that for anion and cation, respectively, x and y the concentrations ; for normal solutions, where the dissociation factor, a, is known, the formula becomes

$$\text{H} = \text{S}^{(1-a)}\text{A}^a\text{K}^a.$$

Assuming that ions of the same mobility have the same viscosity constant, the constants for various ions may be calculated. S may be found by determining H for two different concentrations of the same salt, of known dissociation, by the aid of Arrhenius' formula. When the viscosity coefficients for the various (univalent) ions are thus calculated, and are plotted against the corresponding ionic mobilities, the corresponding points are seen to lie on a curve which may be expressed by the equation

$$\left(\overset{\text{A}}{(\text{K})} - 0.68\right)\overset{\text{U}}{(\text{V})} = \text{const.},$$

where A and K are the viscosity coefficients, and U and V the ionic mobilities. The ions $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ do not obey this relation. This Euler explains by reference to a hypothesis proposed as to the nature of electrolytic dissociation.[3]

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[1] Ztschr. phys. Chem., **25**, 536 (1898).

[2] *Ibid.*, **1**, 285 (1887).

[3] Wied. Ann., **63**, 273 (1894).

Massoulier[1] studied the conductivity of copper sulphate in aqueous solutions of glycerol, and showed that, as the viscosity increases with further addition of glycerol, the resistance of the solution increases proportionately.

Kohlrausch[2] discusses a hypothesis advanced by himself,[3] which puts into more definite form ideas that were previously, and somewhat generally, held. Kohlrausch has shown[4] that, in the case of monovalent ions, the temperature coefficient of ionic mobility is a function of the ionic mobility itself, just as Euler showed the ionic viscosity coefficient to be a function of ionic mobility. The exceptions are the same in both cases, $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$. In the article last mentioned Kohlrausch points out that, if we plot the conductivity curves of various electrolytes in a way to show the variation of conductivity with temperature, and in like manner show the variation of the fluidity of water with change in temperature, all these curves cut the zero axis at about the same point. That is, conductivity and fluidity disappear at the same point. Of course, wide extrapolation is necessary, and this fact must be taken into account. What is more significant, the conductivity curve for certain salts, notably sodium valerate, is almost identical with the fluidity curve. Further, for certain slow moving ions, the temperature coefficient of ionic mobility is almost the same as that of fluidity.

In order to explain these facts, and to avoid the tacit assumption that ionic motion is independent of motion of the solvent, Kohlrausch proposes the hypothesis that "about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion". * * * "The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater dimensions."

This hypothesis accounts for the facts already given: The apparent disappearance of fluidity and conductivity at the same temperature, the coincidence in certain cases of conductivity curve and fluidity curve, the equality of temperature coefficients of ionic mobility and of fluidity, and the fact that the temperature coefficient of ionic mobility is a function of the mobility itself. As stated, the conception of such ionic hydration is not new. We have seen that a similar view was advanced by Stephan, while Ciamician,[1] Nernst,[2] and others attempted by diffusion methods to measure the amount of this hydration in the case of certain negative ions, and came to the conclusion that it must be small. Euler[3] sees in dissociation a combination of ion and solvent—that is, an ionic hydration.

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[1] Compt. rend., **130**, 773 (1900).

[2] Proc. Roy. Soc., **71**, 338 (1903).

[3] Sitz. Ber. Berliner Akad., 1025 (1901).

[4] *Ibid.*, 572 (1902).

The hypothesis of Kohlrausch was proposed for binary electrolytes, at high dilutions, and with water as a solvent. Its application is therefore restricted.

A more general hypothesis, applicable to a series of solvents and to various dilutions, will have to take into account the following factors: First, the viscosity (or fluidity) of the solvent; second, the amount of dissociation in the solution; third, the dissociating power of the solvent. We shall have to find a relation between the dissociating power of the solvent and some constant property of it.

There have been various hypotheses accounting for dissociating power. Nernst[4] finds a connection between dissociating power and the dielectric constant of the solvent. The same relation had been previously pointed out by J. J. Thomson.[5] In general, the higher the dielectric constant of a liquid, the greater is its dissociating power. Thomson, somewhat earlier, showed on theoretical grounds, why we should expect this to be true.

Brühl[6] finds in a condition of unsaturation the cause of the tendency to polymerize, and of dissociating power. He holds the view that oxygen is usually quadrivalent and that water and the alcohols, for example, containing quadrivalent

[1] Ztschr. phys. Chem., **6**, 403 (1890).

[2] Göttingen Nachr., 68, 70, 86 (1900).

[3] Wied. Ann., **63**, 273 (1897).

[4] Ztschr. phys. Chem., **13**, 531 (1894).

[5] Phil. Mag., **36**, 320 (1894).

[6] Ztschr. phys. Chem., **18**, 514 (1895).

oxygen, are unsaturated compounds. Hence their tendency to polymerize and their power to dissociate electrolytes.

The hypothesis of Dutoit and Aston[1] has already been referred to in another connection, and has been shown to hold quantitatively, in certain cases, for water and methyl and ethyl alcohols. We have seen that, for solutions of certain salts in these solvents, the amount of dissociation (as determined from conductivity) is directly proportional to the association factor of the solvent; and, further, that the hypothesis does not apply in the case of acetic acid solutions, nor does it hold for solutions in acetone.

It is plain that the hypothesis of Dutoit and Aston does not go very deeply into the phenomena; all that it asserts is that there is a parallelism between the amount of dissociation effected by the solvent, and the amount of its own association. The two may have no causal connection; the relation may arise simply from the fact that the two properties—amount of dissociation and amount of polymerization—are functions of some other property of the solvent. The Thomson-Nernst hypothesis, however, offers an explanation of very profound significance.

Dutoit and Friderich[2] make an attempt to find a connection between conductivity, viscosity, and association, and thus take a step in the direction of a more general hypothesis. From a study of the conductivities of solutions of different electrolytes in different solvents they came to the following conclusion:

"The values of $\mu\infty$ for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvents, and an indirect function of the coefficient of viscosity of these solvents." The relation was found to hold only in a general way—indeed hardly more than qualitatively.

When we come to consider the proposed relation it is difficult to see why it should exist; that is, it is wholly empirical.

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[1] Compt. rend., **125**, 540 (1897).

[2] Bull. Soc. Chim., (3), **19**, 321 (1898).

It is not in accord with the hypothesis of Dutoit and Aston, for when complete dissociation is reached the association of the solvent is no longer an influencing factor. It is superfluous to discuss the matter further because, as stated, the relation does not hold quantitatively.

This will suffice to indicate what has thus far been done to show a connection between conductivity and viscosity. The relations hitherto brought to light are qualitative. Of far more importance is the establishment of a quantitative relationship. We shall show that such does exist, and we propose the following hypothesis:

The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent. In case the hypothesis of Dutoit and Aston does not hold for the solvent in question, for "association factor of the solvent" must be substituted "amount of dissociation of the solution."

Formulated, the hypothesis is expressed by the relation

$$\frac{\mu_v \eta}{x} = \text{const.} \quad \text{or} \quad \frac{\mu_v \eta}{a} = \text{const.},$$

where the symbols have the usual significance.

This becomes, when $\mu_v = \mu\infty$,

$$\mu_v \eta = \text{const.}$$

The product of μ_v and the coefficient of viscosity is a constant for the same electrolyte in different solvents. Where we use for x, a, the constant is the same throughout.

The meaning of the term "comparable equivalent solutions" needs to be defined. In comparing aqueous solutions those of the same normality (containing equal gram-molecules of electrolyte in equal volumes) are strictly comparable. It is evident that this is not the case when, for example, we come to compare solutions of the same electrolyte in different solvents. In order to be strictly comparable, *the solutions must contain the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of the different solvents*, or equal weights of the (same) electrolyte dissolved in volumes of the solvents which are proportional to the molecular volumes of the solvents in question. That this is the only proper basis of comparison has already been pointed out.

To illustrate, comparable solutions in water and in methyl alcohol would be those containing the same weight of electrolyte dissolved in 18 volumes of water and 40 volumes of methyl alcohol, because the molecular volume of water is 18, and that of methyl alcohol approximately 40. The volumes compared should always be in the ratio 18 (of water) to 40 (of methyl alcohol). Similarly, in the case of methyl and ethyl alcohols, the water would be 40 to 57.5.

We shall now proceed to show that the hypothesis holds. In the first place we have plotted (Fig. VII.) the variation in the fluidity of methyl and ethyl alcohols with temperature, making the different fluidities ordinates, and the different temperatures abscissas. Plotted with these, for the sake of comparison, are the conductivities of various binary electrolytes in solution in the two solvents. Since only two observations were made, one at 0° and the other at 25°, the variation in conductivity is shown by a straight line. If observations at intermediate points could be obtained the line would probably be curved. The first ordinate—that at 0°—is made the same in both examples. The second in the case of the conductivities is then found from the observed value by multiplication by a factor.

From an inspection of the figure (Fig. VII.) it is evident that the lines representing variation of conductivity and variation of fluidity with temperature are almost coincident. That is, the temperature coefficients are almost the same in both, the difference never being over 8 per cent, and in most cases much less than this, particularly for solutions in ethyl alcohol. Völlmer[1] has already called attention to this fact. This amounts, then, to a proof of the Kohlrausch hypothesis for solutions in methyl and ethyl alcohols, and such proof is necessary to establish the validity of our own.

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[1] *Loc. cit.*

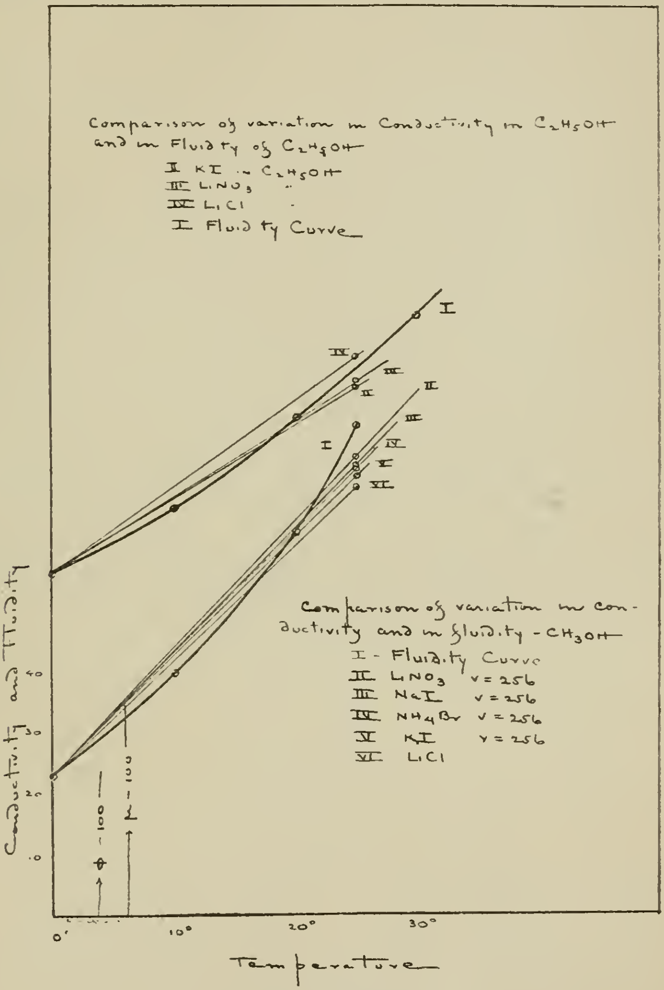

Fig VII

It has already been shown that this is also true for certain electrolytes in certain mixtures of solvents. Though the temperature coefficients of fluidity and conductivity are the same, the value of the quotient $\frac{\mu_v \eta}{a}$ is much greater for an electrolyte in the mixture than for the same electrolyte in the pure alcohol. It is difficult to see why this is the case—unless it be that in the mixture we have a complex solvent not to be compared with the simple one. Certainly the presence of compounds in the mixture would complicate matters. This interesting point needs further investigation.

Knowing the values of the constant for the pure solvent, and assuming the validity of the relation for the mixture, we might calculate the ionic friction. This would not be the same as the coefficient of viscosity of the mixture, but its variation with temperature would be identical.

The next step is the discussion of certain data as to conductivities in the two solvents,—proof that the expression $\frac{\mu_v \eta}{x}$ holds for solutions in these solvents. The values for the coefficients of viscosity have been taken directly, or interpolated from the results of Thorpe and Rodger.[1] The values for the conductivities in the various solvents are taken from observations of Völlmer,[2] Carrara,[2] Jones and Lindsay,[2] and others, and from our own. The values for the association factors are those given by Ramsay and Shields in their first paper,[3] at ordinary temperatures for methyl alcohol, 3.43, for ethyl alcohol, 2.74.

Table LXIX.—$\frac{\mu_v \eta}{x}$ for Lithium Nitrate in Methyl and Ethyl Alcohols.

Volume.	CH_3OH. 0°.	25°.	Volume.	C_2H_5OH. 0°.	25°.
128	0.1288	0.1238	191	0.1239	0.1211
256	0.1353	0.1339	381	0.1368	0.1323
512	0.1484	0.1385	763	0.1500	0.1402

The conductivities compared were for the volumes 128, 256, 512 for methyl alcohol; 190.7, 381.4, 762.8 for ethyl alcohol, these being comparable dilutions. In the case of solutions in ethyl alcohol values for the conductivities were found by interpolation.

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[1] Phil. Trans., **185**, A, 397 (1894).

[2] *Loc. cit.*

[3] Ztschr. phys. Chem., **12**, 433 (1893).

As is seen from inspection of the table, the constants for the comparable volumes are equal to within a few per cent. Further, the constant is the same at the lower and at the higher temperature. Of course, the constants are not the same for the different volumes, for here we have used the association factor as a constant in the equation; it represents dissociation. If we were to substitute per cent of dissociation for the association factor, the values for the constant would be the same in all cases.

Altogether, the agreement of theory and fact is all that could be expected, when we consider the errors involved in the determination of the quantities used. The figures for association are certainly only approximate. Conductivities are liable to an appreciable error, and different observers give values for the viscosity coefficients differing by as much as 4 or 5 per cent.

Table LXX.—$\frac{\mu_v \eta}{x}$ *for Ammonium Bromide in Methyl and Ethyl Alcohols.*

Volume.	CH_3OH. 25°.	C_2H_5OH. 0°.
I.	0.1369	0.1293
II.	0.1441	0.1416
III.	0.1513	0.1531

The volumes of comparison are the same as those in the case of lithium nitrate (Table LXIX.).

Values for the conductivities in ethyl alcohol are taken from the work of Jones and Lindsay; those given by them for methyl alcohol solutions are not used. Those of Carrara are taken, as they agree with values given by Zelinsky and Krapiwin, while those of Jones and Lindsay do not.

In all cases agreement is as close as could be expected.

Table LXXI.—$\frac{\mu_v\eta}{x}$ *for Potassium Iodide in Methyl and Ethyl Alcohols.*

Volume.	CH_3OH. 25°. Jones and Lindsay.	CH_3OH. 25°. Carrara.	CH_3OH. 0°. Jones and Lindsay.	C_2H_5OH. 25°. Jones and Lindsay.	C_2H_5OH. 0°. Jones and Lindsay.	$\frac{\mu_v\eta}{\alpha}$ CH_3OH.	$\frac{\mu_v\eta}{\alpha}$ C_2H_5OH.
I.	0.1377	0.1308	0.1417	0.1298	0.1359		
II.	0.1471	0.1408	0.1526	0.1428	0.1479	0.516	0.571
III.	0.1558	0.1466	0.1617	0.1544	0.1592	0.525	
IV.	0.1636	0.1513	0.1665	0.1698	0.176	0.539	0.571
∞						0.539	0.571

The volumes compared were 64, 128, 256, and 512 for methyl alcohol; for ethyl alcohol, 95.7, etc. Both Jones and Lindsay's and Carrara's values for conductivities in methyl alcohol were used in order to compare the results. In some cases those of the one give better agreement, in other cases those of the other, indicating that the differences are influenced by experimental error.

It should be stated that in this case Gartenmeister's[1] values for the coefficients of viscosity were used. The calculations were made before we decided to use those given by Thorpe and Rodger. It would hardly be profitable to recalculate, since the result is a constant whichever set of values be employed. We have satisfied ourselves of this by numerous trials. In many cases three or four calculations have been made, using the different constants given in the tables of Landolt and Boernstein.

Table LXXII.—$\frac{\mu_v\eta}{x}$ *for Lithium Chloride in Methyl, Ethyl, and Propyl Alcohols.*

Volume.	CH_3OH. 25°.	C_2H_5OH. 18°.	C_3H_7OH. 15°.	
I.	0.1213	0.1256	0.1164	
	0.1166			Völlmer—18°

The volumes compared are 256, 403, 604. The values for the conductivities are taken from the work of Carrara and Völlmer, and for *n*-propyl alcohol from Schlamp.[2] The agreement is satisfactory.

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[1] Landolt and Boernstein's Tabellen.

[2] Ztschr. phys. Chem., **14**, 274 (1894).

It is interesting to note that the relation holds for picric acid in solution in methyl and ethyl alcohol. Where the volumes compared are 205 and 270, respectively, $\frac{\mu_v \eta}{x}$ in the one case equals 0.0665, and in the other, 0.0641. The data for the comparison are furnished by Schall.[1]

Other results may be summarized without going further into detail.

Table LXXIII.— $\frac{\mu_v \eta}{x}$ *for Various Electrolytes in Different Solvents.*

	CH_3OH.	C_2H_5OH.	*n*-C_3H_7OH.	
NaI	0.1438	0.1447		Jones and Carroll(25°) Völlmer(18°)
$v = 200, 283$				
$v = 750, 575$	0.157		0.159	Jones and Carroll(25°) Schlamp(15°)
CH_3COONa	0.1156			Völlmer(18°)
$v = 832, 1200$	0.1123	0.1093		Carrara(25°) Völlmer(18°)
CH_3COOK	0.1279	0.1247		Völlmer(18°)
NaCl				
$v = 228, 340$	0.1457	0.1366		Carrara(25°) Völlmer(18°)

In all these instances the agreement continues to be satisfactory.

In the foregoing pages we have discussed all the material available in the literature. In all of the cases—some nine in number—fact and theory are in accord. It can, therefore, be fairly claimed that the proposed hypothesis thus becomes highly probable. Further investigation is, however, desirable, to see how widely it applies.

For solutions in which dissociation is complete the formulated hypothesis becomes $\mu\eta =$ const. The proof of the validity of this relation is, it seems to us, a crucial test. We give in the following table the necessary comparisons :

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[1] Ztschr. phys. Chem., **14**, 707 (1894).

Table LXXIV.—$\mu_v \eta$ for Various Electrolytes in Various Solvents.

Electrolyte.	C_2H_5OH. $n = 0.012385$. 18°.	CH_3OH. $n = 0.00666$ (18°). 0.00552 (25°).	CH_3COCH_3. $n = 0.00353$. 25°.	n-C_3H_7OH. $n = 0.002554$. 15°.
KI	0.567	0.530—18° 0.528—25°	0.541	
NaI	0.466	0.505—18° 0.496—25°	0.481	
NH_4I		0.581	0.538	
LiCl	0.377	0.416—18° 0.427—25°		
NaCl	0.434	0.479		

The values for acetone were taken from the work of Carrara,[1] those for ethyl alcohol from that of Völlmer, those for methyl alcohol from that of Völlmer and Carrara, and those for propyl alcohol from the investigation of Schlamp.

When we consider the necessarily large experimental error involved in the determination of the limiting values for conductivity—an error which must certainly be greater than that involved in the determination of conductivities at ordinary dilutions—the agreement is as good as could be expected. Further, for lithium and sodium chlorides in ethyl alcohol, limiting values were probably not reached, for with them Völlmer did not go to a dilution as high as in other cases. The constants for these salts would probably be greater than the values given in the table, thus making a still better agreement.

Summary and Conclusions.

1. The investigations of Zelinsky and Krapiwin, and of Jones and Lindsay, have been extended, and the occurrence of the minimum in conductivity has been shown for three substances—cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water.

2. The dissociation (as determined from conductivity) of sodium and potassium iodide, and potassium bromide in 50 per cent methyl alcohol, has been determined and has been found to be greater than that in water at the corresponding dilution.

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[1] Gazz. Chim. Ital., **27**, I., 207 (1897).

3. It has been shown that the explanation of the minimum in conductivity offered by Jones and Lindsay is not entirely satisfactory. The phenomenon has been shown to be dependent primarily upon the decrease in fluidity which results when the liquids are mixed.

4. The hypothesis of Dutoit and Aston has been proved quantitatively for certain salts in three solvents—water, methyl alcohol, and ethyl alcohol.

5. The hypothesis of Kohlrausch (formation of an atmosphere of the solvent around the ions in solution) has been shown to hold for binary electrolytes in methyl and ethyl alcohols.

6. A hypothesis correlating conductivity, association, and viscosity (or fluidity) has been proposed, and has been shown to hold for all the cases available for discussion.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1904.

SOME REACTIONS OF BENZOIN.

BY J. B. GARNER.

A study of the results of the interaction of benzoin and alcoholic potassium hydroxide or sodium ethylate, under varying conditions of concentration, time, and temperature, has been made by several investigators. Each succeeding study of the subject has resulted, in a measure, in the development of facts which have simplified previous interpretations of the reaction. The confusion regarding the exact nature of this reaction has, nevertheless, been considerable.[1]

Epitome of Previous Work.

Zinin,[2] who was the first to investigate the reaction under discussion, found that benzoin, when treated for fifteen hours at a temperature of 160° to 170° with a solution of potassium hydroxide (approximately 14 per cent) in ethyl alcohol (92 per cent), underwent chemical change which resulted in the formation, as chief products of the reaction, of hydrobenzoin, benzilic acid (associated with some benzoic acid), needle-like crystals (which were not investigated) and an oily substance supposed to be benzyl alcohol.

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[1] "Handbuch der organischen Chemie," Beilstein Auflage III., S. 222.

[2] J. prakt. Chem., 98, 495.

Jena and Limpricht[1] took up the study where Zinin left off and, by six series of experiments, showed that the reaction did not progress as smoothly as Zinin had stated. In the first series benzoin was heated in a flask with a return-condenser, on a water-bath, for three hours, with an alcoholic solution of potassium hydroxide. Benzoic acid, traces of benzilic acid, benzoin ether, and a substance $C_{28}H_{24}O_5$, melting at 61°, were the only products. No details were given as to the methods which were used in separating and identifying the compounds. The authors themselves expressed doubt as to the correctness of their analyses of the substance for which they assigned the formula $C_{28}H_{24}O_5$.

The five remaining series of experiments with benzoin were carried out in sealed tubes so as to prevent access of air. In the second and sixth series reactions were carried out with benzoin and alcoholic potassium hydroxide, the time, temperature, and concentration being varied. In the second series, benzoin was heated for twelve hours at 100° with dilute alcoholic potassium hydroxide. Hydrobenzoin, a substance called ethylbenzoin (m. p. 95°), and isodesoxybenzoin pinacone (m. p. 62°) were obtained in addition to the products of the first series of experiments. The authors found, further, that isodesoxybenzoin pinacone, when distilled with dilute sulphuric acid, decomposed into two substances—one was readily soluble in hot alcohol, and the other only with difficulty. The former was found to melt at 108°, and as a result of an analysis was assigned the formula $C_{28}H_{24}O$. It was, therefore, concluded that its formation was due to the loss of water by isodesoxybenzoin pinacone under the influence of the dilute sulphuric acid. The second substance melted, when pure, at 190°. It was not investigated.

In the third, fourth, and fifth series of experiments reactions were carried out with benzoin and alcoholic solutions of sodium ethylate. The quantity of benzoin, the time, and the temperature were varied, but the amount of sodium ethylate was kept constant. In the fourth series the concentration of benzoin was twice as great as in the third series, the time was only one-sixth as long, and the temperature was 50° higher, yet the results were the same in both series. Hydrobenzoin, ethylbenzoin, isodesoxybenzoin pinacone, and ethylbenzilic acid were the products of the reaction. No traces of benzoic acid and benzilic acid were found.[1]

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[1] Ann. Chem. (Liebig), **155**, 93.

The conditions of the fifth series differed from those of the fourth series only in the time and temperature of the reaction. The products found differed from those of the fourth series, as follows: stilbene, benzoic acid, and hydrogen were found in place of hydrobenzoin. These substances were assumed to have resulted from the decomposition of hydrobenzoin by the interaction with sodium ethylate at the temperature used. The other products were the same as in the fourth series. No reliable details were given as to the methods used in the identification of stilbene and hydrogen.

Limpricht and Schwanert,[2] in repeating the work of Jena[3] on the action of ethyl alcohol upon benzil, found that the substance called tolane alcohol, and assigned the formula $C_{14}H_{12}O_2$ by Jena, owed its formation to the interaction of ethyl alcohol and benzoin. Benzoin must have been contained as an impurity in the benzil which Jena used. These investigators regarded it as a benzoin derivative and gave to it the formula $C_{30}H_{26}O_4$ and the name ethyldibenzoin. By treating pure benzoin with alcoholic potassium hydroxide in the presence of air, Limpricht and Schwanert readily obtained the substance, but no analyses were made. The solubilities were determined, an acetyl derivative (m. p. 145°) was prepared, and the fact was established that the substance did not yield benzil when it was treated with nitric acid.

In 1885 Japp and Owens,[4] in a paper on "Condensations of Benzil with Ethyl Alcohol," criticized the work of Limpricht and Schwanert. They claimed to have obtained a 60 per

[1] Ann. Chem. (Liebig), **155**, 96.

[2] Ber. d. chem. Ges., **4**, 335.

[3] Ann. Chem. (Liebig), **155**, 79.

[4] Ber. d. chem. Ges., **15**, 175.

cent yield of ethyldibenzoin by the continued action of cold dilute alcoholic potassium hydroxide upon carefully purified benzil. They therefore viewed the substance as a derivative of benzil and named it ethyldibenzil. In support of their view, in addition to its method of preparation, they submitted analyses which led them to assign to it the formula $C_{30}H_{24}O_4$, which formula differed from that of Limpricht and Schwanert by two hydrogen atoms. Japp and Owens were unable to prepare the acetyl derivative melting at 145°. They attempted to explain the differences between their results and those of Limpricht and Schwanert by the following: (1) That it was not taken into consideration that benzoin in the presence of air was converted into benzil by the action of alcoholic potassium hydroxide; (2) that it was not observed that the supposed ethyldibenzoin had alcohol of crystallization; and (3) that the acetyl derivative, instead of being a pure substance, was a mixture, as the melting-point varied from 130° to 200°. A doubt was also expressed regarding the existence of a true acetyl derivative, as no details had been published as to methods used in its preparation. No explanation was, however, made of the fact that ethyldibenzil, which was said to have alcohol of crystallization, could be recrystallized from benzene and its melting-point remained unchanged.[1]

In attempting to prepare the alkylbenzoins by the interaction of benzoin, sodium ethylate, and alkyl iodides, Päpcke[2] noticed that when pure benzoin was dissolved in boiling absolute ethyl alcohol, and a solution of sodium ethylate in absolute ethyl alcohol was added to it, an intense brownish-violet coloration was produced and in a few seconds the hot solution solidified to a mass of blue crystals, which, when heated, became colorless, but upon shaking in contact with air, again became colored. To these crystals were added alkyl iodides, in the hope that alkyl benzoins, analogous to the alkyl desoxybenzoins of V. Meyer,[3] might be formed, but no alkyl benzoins were obtained. Päpcke attempted to show that the product formed by the interaction of sodium ethylate and benzoin was a result of the displacement of one hydrogen in the secondary alcoholic grouping by one atom of sodium. In this connection he said : "In all cases the sodium content was found to be significantly different from that demanded by the formula,

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[1] "Handbuch der organischen Chemie," Beilstein Auflage III., s. 283.

[2] Ber. d. chem. Ges., **21**, 1335-6.

[3] *Ibid.*, **20**, 2944.

$$C_6H_5—CO—CH(ONa)—C_6H_5,$$

although this formula is the most probable one." His results, coupled with those of Meyer, clearly established that the action of sodium ethylate upon desoxybenzoin was of an entirely different order from that of the action of sodium ethylate upon benzoin. Päpcke endeavored to prepare ethylbenzoin by the method of Jena[1] but found that he was unable to do so because, as he said : "The yield was so small and the product so difficult to isolate and purify."

Klinger[2] claimed to have established that dilute aqueous potassium hydroxide, in the presence of air, reacts incompletely and slowly with benzoin to produce benzaldehyde, benzhydrol, benzoic, and benzilic acids, while in the presence of air or oxygen it produces rapidly, and almost quantitatively, benzilic acid and some benzoic acid. The results of Klinger's experiments in the absence of air can be interpreted only upon the assumption that oxygen or air was really present, for Knoevenagel and Arndt[3] have conclusively shown that aqueous potassium hydroxide, of concentrations up to 30 per cent., at a temperature of 100°, in the absence of oxygen or air, has no action upon benzoin. With very concentrated aqueous potassium hydroxide, under varying conditions of concentration and temperature, benzoin reacts to produce benzoic acid and benzyl alcohol, or products resulting from the interaction of benzyl alcohol and part of the unchanged benzoin, due to the different conditions of the various experiments. These authors based the interpretation of their results upon the assumption that benzoin undergoes hydrolytic dissociation, analogous to the so-called acid decomposition in the acetoacetic ether series, into benzyl alcohol and benzoic acid.

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[1] Ann. Chem. (Liebig), **155**, 97.

[2] Ber. d. chem. Ges., **19**, 1868.

[3] *Ibid.*, **35**, 1985.

Objects of the Investigation.

The present investigation of the reaction which takes place between benzoin and alcoholic solutions of sodium ethylate, has been undertaken for the following purposes:

1. To establish the composition and constitution of the crystalline substance, observed by Päpcke,[1] which results when absolute ethyl alcoholic solutions of benzoin and sodium ethylate are brought together at 25°.

2. To determine quantitatively the exact nature of the reactions which take place when benzoin is treated with solutions of sodium ethylate in ethyl alcohol, (*a*) of 92 per cent., as formerly carried out by Jena and Limpricht[2]; and (*b*) absolute; a comparison of the results obtained might then lead to an interpretation of the reactions involved.

EXPERIMENTAL PART.

Benzoin with Sodium Ethylate at 25°.

One molecule (5 grams) of carefully purified benzoin of melting-point 134° was dissolved in absolute ethyl alcohol (75 cc.) and allowed to cool to about 25°; then a solution of one atom of sodium (0.6 gram), in absolute ethyl alcohol (75 cc.), was added. The mixture immediately became brownish-violet in color, and in a few minutes the whole solidified to a mass of long, white, silky needles. By filtering rapidly, washing well with absolute alcohol and absolute ether, and transferring to a vacuum desiccator, decomposition, due to the action of moist air, was avoided. After drying for thirty-six hours over concentrated sulphuric acid, *in vacuo*, the following analyses were obtained:

I. 0.1320 gram gave 0.3594 gram CO_2 and 0.0641 gram H_2O.

II. 0.1722 gram gave 0.4726 gram CO_2 and 0.0829 gram H_2O.

III. 0.2456 gram digested in water at 25° for thirty minutes required 36.12 cc. N/50 H_2SO_4, methyl orange used as indicator.

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[1] Ber. d. chem. Ges., **21**, 1335.

[2] Ann. Chem. (Liebig), **155**, 93.

IV. 0.3123 gram analyzed as in III., required 43.7 cc. N/50 H_2SO_4.

V. 0.4522 gram gave 0.0832 gram Na_2SO_4.

	Calculated for $C_{42}H_{32}O_5Na_2$.	Found.				
		I.	II.	III.	IV.	V.
C	74.32	74.25	74.84	....	....	....
H	4.83	5.39	5.35	....	....	....
Na	6.79	....	....	6.76	6.48	5.97

The product is decomposed by almost all of the ordinary solvents. It appears to be stable only in cold absolute ethyl alcohol and absolute ether, in the absence of air and moisture. Its decomposition, when treated with water at 20°, is very interesting and is the most important method of determining its constitution. This reaction has been studied both qualitatively and quantitatively. For the purposes of qualitative study, the following experiment was carried out: A mixture of the substance (5 grams), as prepared for analysis, and water (50 grams), was heated for one-half hour in a flask, in the water-bath, at 20°. The white solid substance remaining was filtered off, and both solid and filtrate were carefully examined. The solid possessed all of the solubilities and physical properties of benzoin, and readily formed acetyl benzoin with acetyl chloride; benzil, with nitric acid, and reduced aqueous alcoholic Fehling's solution. The filtrate was alkaline in reaction, as shown by treatment with phenolphthaleïn, litmus, etc. When acidified with dilute sulphuric acid, a white solid separated which was rigidly identified as benzoic acid. Other portions of the filtrate were tested for ethyl alcohol, (1) by means of iodine and potassium hydroxide, and (2) by means of a mixture of dilute sulphuric acid and potassium chromate, but each time the results were negative. The failure of the chromic acid to react with the filtrate established the fact that benzyl alcohol was absent.

For the purposes of quantitative study, the following experiment was carried out: 0.3123 gram of substance was heated with 32 cc. of water for one-half hour at 20°; the solid remaining was filtered off and washed with cold water until the wash-waters were free from sodium hydroxide and benzoic acid. The residue was dried in an air-bath at 110°, to constant weight. 0.2008 gram of benzoin was left. The filtrate from benzoin was titrated with N/50 sulphuric acid, methyl orange being used as indicator, and it was found that 43.7 cc. of the acid were required for neutralization. The substance, therefore, had decomposed into benzoin (64.3 per cent), sodium hydroxide (calculated as Na 6.48 per cent) and benzoic acid.

The decomposition which takes place when the substance is treated with glacial acetic acid results in the formation of benzoin, benzoic acid, and sodium acetate.

Benzoin with Sodium Ethylate.

A. Jena and Limpricht's[1] experiment was repeated. Ethyl alcohol (92 per cent) was used as solvent and in the preparation of the sodium ethylate.

In order to be able to study this reaction, two mixtures each of benzoin (8 grams), and a solution of sodium (2 grams), in ethyl alcohol (40 cc. of 92 per cent), were heated in sealed tubes, for six hours, at 150° to 160°. On opening the tubes, the yellow, semi-solid contents were found to be under no excess of pressure. Both masses were transferred to a distilling-flask and practically all of the alcohol was removed by heating in the water-bath. The residue was almost odorless. It was digested in the cold with water for several hours, and an insoluble residue was removed by filtration. This was dissolved in ether and shaken up with solutions of sodium carbonate and sodium hydroxide to insure the complete removal of any acidic substances. The ethereal solution was then dried over calcium chloride and the ether was distilled. A yellowish crystalline solid (m. p. 62° to 63°) remained which was readily soluble in hot alcohol, cold ether, and chloroform, less so in hot benzene, and very sparingly in hot ligroin (b. p. 40° to 60°). These solubilities were made use of in separating the compounds present. By dissolving the mixture in a small amount of hot alcohol and cooling the solution, crystals separated which were thoroughly identified as isohydrobenzoin (m. p. 119°.5).[2]

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[1] Ann. Chem. (Liebig), **155**, 94.

[2] *Ibid.*, **198**, 154.

The alcohol in the filtrate was removed by distillation on the water-bath, and the residue dissolved in much hot ligroin; crystals immediately separated, which were identified as the dimolecular anhydride of isohydrobenzoin (m. p. 102°).[1] The filtrate from this substance, upon standing for several days at about 0°, deposited exceedingly large prismatic crystals, which melted at 62°. It was identical in properties with ethylbenzoin as prepared by Fischer's method;[2] 1.75 grams of ethylbenzoin and 3 grams of a mixture of about equal quantities of isohydrobenzoin and its dimolecular anhydride were obtained as an average of several experiments when 8 grams of benzoin were used.

The aqueous alkaline filtrate, from the mixture of ethylbenzoin, etc., was acidified with dilute sulphuric acid and the mixture extracted repeatedly with ether. The ethereal extract was shaken up with solutions of sodium carbonate and sodium hydroxide. The neutral solution remaining was dried over calcium chloride, and the ether removed by distillation. The oily residue was found to weigh 4.8 grams. By fractionation, 1.9 grams of pure benzyl alcohol (b. p. 208°) were obtained; it was identified by its ready conversion into benzaldehyde when treated with nitric acid. The remainder left in the distilling-flask was shown to be a mixture of hydrobenzoin and the dimolecular anhydrides of hydrobenzoin and isohydrobenzoin. The presence here of these last three substances may be explained by the fact that, in the presence of benzyl alcohol, they are soluble in water to a considerable extent. The sodium carbonate and sodium hydroxide solutions were acidified with dilute sulphuric acid and extracted with ether. Upon drying and removal of the ether a semi-solid residue (6.3 grams) was obtained from the sodium carbonate solution, and a yellowish oil (0.15 gram) from the sodium hydroxide solution. The residue from the sodium carbonate was boiled repeatedly with water and filtered through a hot-water funnel to remove benzoic and benzilic acids. These were separated by fractional recrystallization from hot ligroin (b. p. 40° to 60°) in which benzoic acid is readily soluble, and benzilic acid is only very slightly so. Both acids were thoroughly identified. Of benzoic acid there were 2.2 grams, and of benzilic acid less than 0.1 gram. After the removal of benzoic and benzilic acids, 4.2 grams of a yellow, honey-like substance remained, of which the composition and constitution are doubtful. Upon analysis, widely varying results were obtained. It is probably the so-called ethylbenzilic acid of Jena and Limpricht.[1] It possessed most of the properties attributed to that substance. There was, however, a notable exception. Jena and Limpricht found that the so-called ethylbenzilic acid distilled unchanged. It has been found by me to decompose violently with the evolution of carbon dioxide when heated to 70° and to form a dark-red, viscous oil. On heating this oil to 260°, a very small quantity of benzoic acid distilled off, and when the temperature was raised, charring began and little or nothing passed over below 360°.

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[1] Ann. Chem. (Liebig), 198, 160.

[2] Ber. d. chem. Ges., 26, 2415.

The following results are typical of the yields which were obtained when 16 grams of benzoin were used :

Ethylbenzoin	1.75
Hydrobenzoin, isohydrobenzoin, and their dimolecular anhydrides	4.9
Benzyl alcohol	1.9
Benzoic acid	2.2
Benzilic acid, about	0.1
Ethylbenzilic acid	4.2
	15.05

B. Ethyl alcohol (specific gravity 0.796 at 16°.5) was used as solvent and in the preparation of sodium ethylate.

To a solution of 1 molecule of benzoin (15 grams) in ethyl alcohol (225 cc.) a solution of one atom of sodium (1.8 grams) in ethyl alcohol (175 cc.) was added. The mixture was allowed to solidify and then was boiled in a water-bath for twenty-six hours, using a reflux condenser. During the boiling, the mixture slowly changed color, from brownish-violet to pale yellow, and all of the solid went into solution.

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[1] Ann. Chem. (Liebig), **155**, 100.

The end of the reaction was not reached until these conditions were realized. The alcohol was completely distilled and the yellow solid remaining thoroughly digested with cold water (500 cc.). The insoluble portion (5.2 grams) was filtered and proved to be a mixtûre of hydrobenzoin and isohydrobenzoin. These two substances were separated by fractional recrystallization from hot benzene. Hydrobenzoin is less soluble than isohydrobenzoin in this solvent, and separates in large monoclinic crystals, which are almost pure, from a solution of the mixture, while isohydrobenzoin only separates readily after hydrobenzoin has been removed and the filtrate considerably concentrated. Two-thirds of the mixture was hydrobenzoin and the remainder isohydrobenzoin.

The aqueous filtrate from the mixture of hydrobenzoin and isohydrobenzoin was strongly alkaline. It was extracted with ether and the extract dried over calcium chloride. On removing the ether, the residue (2.6 grams) solidified. It was made up of hydrobenzoin (0.8 gram), isohydrobenzoin (0.4 gram), the dimolecular anhydride of hydrobenzoin (0.8 gram), and the dimolecular anhydride of isohydrobenzoin (0.5 gram). These substances were separated from one another by making use of their differences in solubility in hot benzene, alcohol, and ligroin (b. p. 40° to 60°). On acidifying the cold alkaline aqueous residue from the ether extract, a copious cream-like precipitate (7.2 grams) was obtained which consisted of benzoic (1.2 grams), traces of benzilic acid, ethylbenzilic acid (4.9 grams), and α-benzoyl-α-phenyl-α'-oxy-β-phenyltetrahydrofurfurane (1.9 grams, *vide infra*). These substances were separated from one another in the following way: The mixed precipitate was repeatedly boiled in water and filtered through a hot-water funnel. The filtrate was cooled and extracted with ether; the ethereal extract was dried over calcium chloride and the ether removed by distillation. Benzoic and benzilic acids remained and were separated by fractional recrystallization from hot ligroin (b. p. 40° to 60°). The residue from hot water was dissolved in hot ethyl alcohol. This solution, on cooling, deposited large prismatic crystals of the tetrahydrofurfurane derivative.

Upon evaporation of the alcoholic filtrate, the so-called ethylbenzilic acid was left as a honey-like substance.

The following results are typical of the yields which were obtained when 15 grams of benzoin were used.

Hydrobenzoin	4.2
Isohydrobenzoin	2.2
Dimolecular anhydride of hydrobenzoin	0.8
Dimolecular anhydride of isohydrobenzoin	0.5
Benzoic acid	2.2
Benzilic acid	trace
Ethylbenzilic acid	4.9
Tetrahydrofurfurane derivative	1.9
	15.7

Benzoin with Sodium Ethylate and Oxygen at 90°.

Ethyl alcohol (sp. gr. 0.796 at 16°.5) was used as solvent and in the preparation of the sodium ethylate. The oxygen was dried and purified by passing through concentrated sulphuric acid and over solid potassium hydroxide and soda-lime.

To a solution of 1 molecule of benzoin (15 grams) in ethyl alcohol (225 cc.), a solution of 1 atom of sodium (1.8 grams) in ethyl alcohol (175 cc.) was added. The brownish-violet mixture was allowed to solidify, and then was boiled in a water-bath for twenty-three hours, using a reflux-condenser. During the boiling, pure, dry oxygen was passed into the mixture. For the first three hours the mixture was brownish-violet in color, afterwards the color was yellow; upon this substance oxygen seemed to have little or no effect. If the tube carrying the oxygen should, by chance, become plugged before the end of three hours, by the entrance into it of some solid from the mixture, the latter would become yellow, but the brownish-violet color could be immediately restored by the introduction of oxygen. The reaction was complete when all of the solid was in solution. The mixture resulting was examined as in Series *B*. The results of a typical case were as follows: In the neutral portion, benzaldehyde (2.5 grams) and the tetrahydrofurfurane derivative (1.7 grams) were found. The acidic portion contained benzoic acid (8.8 grams), the tetrahydrofurfurane derivative (1.9 grams), and traces of benzilic acid.

Discussion.

From the facts obtained from the study of the action of sodium ethylate upon benzoin at 25°, it seems quite clear that the substance first formed cannot be an addition-product of benzoin, analogous to the one obtained by Claisen,[1] from the interaction of benzaldehyde and sodium ethylate, for Claisen has shown conclusively that, when the addition-product is treated with water, ethyl alcohol is formed as one of the decomposition products, and that benzaldehyde, which was originally present, is converted quantitatively into benzyl alcohol and benzoic acid by its interaction with sodium hydroxide. Claisen remarked, in this connection, that the results of the decomposition are the same as those which are obtainable by the interaction of benzaldehyde and aqueous sodium hydroxide alone. It is equally clear that the substance cannot have a constitution analogous to that of sodium desoxybenzoin,[2] or of sodium acetoacetic ether, for the reasons, (1) that Päpcke[3] was unable to prepare the alkyl benzoins by the treatment of the substance with alkyl iodides, and (2) that, since E. Fischer[4] has prepared the alkyl benzoins by the condensation of benzoin and the various alcohols with hydrogen chloride, and has found them to be stable substances in the presence of sodium hydroxide, the intermediate formation and subsequent decomposition of the alkyl benzoins could not be assumed.

The decomposition of the crystalline substance, under the influence of water and air, into benzoin, benzoic acid, and sodium hydroxide, when considered together with its analysis, argues very strongly in favor of the following constitution :

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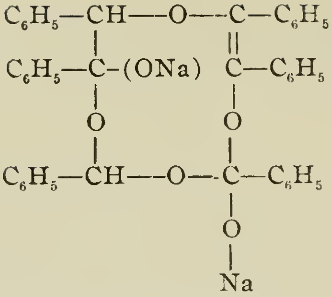
[1] Ber. d. chem. Ges., **20**, 646.

[2] *Ibid.*, **21**, 1297.

[3] *Ibid.*, **21**, 1335.

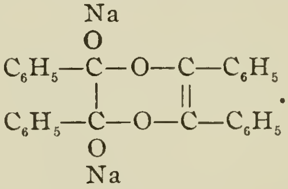
[4] *Ibid.*, **26**, 2413.



The equation representing the reaction is as follows :

$$C_{42}H_{32}O_5Na_2 + 3H_2O + 2O = 2C_{14}H_{12}O_2 + 2C_7H_6O_2 + 2NaOH.$$

The assumption of the formation of a substance with the above constitutional formula is in a measure justified by the work of Beckmann, Paul,[1] and Nef.[2] The latter investigator has shown that the substance resulting from the interaction of benzil and sodium, in absolute ether solution, has the constitution represented by the following formula :



In view of Nef's work, the thought was justified that, since benzoin is so easily oxidized to benzil, the sodium benzil compound might possibly have been formed instead of the substance to which I have assigned the formula given above. In order to establish rigidly that the substance is not the sodium compound of benzil, the following experiment was carried out : Fifteen grams of the crystalline substance were mixed with 250 cc. of absolute ether, and to this were added 11 grams of benzoyl chloride. The whole mixture was heated in the water-bath until there was no further change. The solid which remained was filtered off and was identified as benzoin. The ethereal solution was set aside, and after standing over night deposited more benzoin. After removal of benzoin, the ether was distilled, and the residue examined and found to contain benzoic acid and unchanged benzoyl chloride. Not a trace of isobenzil or benzil could be detected.

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[1] Ann. Chem. (Liebig), **266**, 1-28.

[2] *Ibid.*, **308**, 284-292.

The results of the interaction of benzoin and sodium ethylate in Series *A* and *B* are as follows :

Series A.

Ethylbenzoin	1.75
Hydrobenzoin, isohydrobenzoin, and their dimolecular anhydrides	4.9
Benzoic acid	2.2
Benzilic acid	0.1
Ethylbenzilic acid	4.2
Benzyl alcohol	1.9
	15.05

Series B.

Ethylbenzoin	..
Hydrobenzoin, isohydrobenzoin, and their dimolecular anhydrides	7.7
Benzoic acid	2.2
Benzilic acid	trace
Ethylbenzilic acid	4.9
Benzyl alcohol	..
Tetrahydrofurfurane derivative	1.9
	15.70

The above tabulation of results shows that three reactions have taken place side by side in Series *B*: (1) The substance $C_{42}H_{32}O_5Na_2$ has been formed by the interaction of benzoin and sodium ethylate; (2) this substance has reacted with ethyl alcohol and traces of water, under the influence of sodium ethylate, to produce almost molecular quantities of hydrobenzoin, etc., benzilbenzoin (intermediate product), and acetaldehyde; (3) benzilbenzoin has then reacted (*a*) with alcohol to produce ethylbenzilic acid, benzoin, and benzaldehyde; (*b*) the mixture of benzoin, benzaldehyde, and acetaldehyde, under the influence of sodium ethylate, has reacted to produce the tetrahydrofurfurane derivative; and (*c*) the remaining benzaldehyde has been oxidized to benzoic acid by the action of the oxygen of the air.

The following equations are representative of the reactions which have taken place:

$$1.\quad 3C_{14}H_{12}O_2 + 2NaOC_2H_5 = C_{42}H_{32}O_5Na_2 + 2C_2H_5OH + H_2O;$$

$$2.\quad 2C_{42}H_{32}O_5Na_2 + 6H_2O + CH_3\text{—}CH_2OH = \underset{\text{(Benzilbenzoin.)}}{C_{42}H_{32}O_6} + \underset{\text{(Hydrobenzoin.)}}{3C_{14}H_{14}O_2} + 4NaOH + \underset{\text{(Aldehyde.)}}{CH_3CHO};$$

$$3.\quad (a)\ 2C_{42}H_{32}O_6 + 4C_2H_5OH = 4C_{16}H_{16}O_3 + C_{14}H_{12}O_2 + 2C_7H_6O;$$

$$(b)\ C_{14}H_{12}O_2 + C_7H_6O + CH_3CHO = C_{23}H_{20}O_3 + H_2O;$$

$$(c)\ C_7H_6O + O = C_7H_6O_2.$$

These conclusions are justified by the experimental results and by the observations of Klinger,[1] who has shown (1) that when benzil, in an aqueous ethereal solution, is exposed to direct sunlight it undergoes changes which result in the formation of benzilbenzoin, acetaldehyde, and traces of benzoic and benzilic acids; (2) that benzilbenzoin, when treated for an hour with an aqueous solution of potassium hydroxide (4 per cent), is converted into benzil, benzoin, benzaldehyde, benzilic acid, and some benzoic acid; (3) that benzilbenzoin, when heated with aqueous potassium hydroxide (5 per cent) until all of the yellow drops of benzil have gone into solution, is converted into benzilic acid to the extent of 63.6 per cent. The other product is benzoin (36.4 per cent).

In Series *A*, the same three reactions have taken place as in Series *B*, but to a less extent. The differences are due undoubtedly to the presence of 8 per cent of water in the ethyl alcohol used in Series *A*. This water has reacted with sodium ethylate and produced sodium hydroxide in relatively large quantity. Ethylbenzoin has resulted from the replacement of the alcoholic hydrogen in the secondary alcoholic grouping in benzoin by the ethyl radical.[1] The presence of benzyl alcohol, and a relatively large amount of benzoic acid, indicates (1) that the decomposition of benzilbenzoin into benzaldehyde, etc., which was first observed by Klinger,[2] has taken place to a greater extent in Series *A* than in Series *B*; and (2) that, on account of the presence in the mixture of a considerable quantity of sodium hydroxide, the benzaldehyde has undergone hydrolysis, producing benzoic acid and benzyl alcohol.

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[1] Ber. d. chem. Ges., 19, 1864.

The direction of the reaction which takes place between benzoin and sodium ethylate when oxygen is present in large quantities, has been changed considerably from that of Series *B*. Reactions (1), (2), and (3) *b* and *c* of Series *B* have taken place, while reaction (3) *a* has not. The absence of hydrobenzoin, and the presence of benzaldehyde and a relatively large amount of benzoic acid in quantity almost equivalent to that of hydrobenzoin, etc., in Series *B*, can be explained by the fact that hydrobenzoin is easily oxidized to benzaldehyde. Auwers[3] has shown that the hydrobenzoins and their dimolecular anhydrides are readily oxidized by chromic acid, or dilute potassium permanganate, to benzaldehyde. Oxygen, in the presence of sodium ethylate, has oxidized hydrobenzoin to a mixture of benzaldehyde and benzoic acid. As oxygen seemed to have little or no effect after the first three hours' boiling of the mixture, and as the reaction required twenty-three hours for completion, it appears very probable that the view expressed regarding the course of the reactions in Series *B*, is the correct one.

It will also be noted that the present study has resulted in the establishment of the following facts: (1) that the so-called ethylbenzoin of Jena and Limpricht[4] is a mixture of hydrobenzoin, isohydrobenzoin, and their dimolecular anhydrides. Jena and Limpricht state that the substance which they obtained is oxidized by nitric acid to benzoin, and is not affected by sodium amalgam. These two reactions agree with the well-known reactions of hydrobenzoin, etc., as shown by Auwers.[1] E. Fischer[2] has shown that the alkyl benzoins are readily oxidized by nitric acid to benzil ; (2) that the so-called isodesoxybenzoinpinacone of Jena and Limpricht[3] is a mixture of ethylbenzoin, isohydrobenzoin, and its dimolecular anhydride ; (3) that the so-called ethyldibenzoin of Jena,[4] Limpricht and Schwanert,[5] Jena and Limpricht,[6] and Japp and Owen,[7] is *α*-benzoyl-*α*-phenyl-*α*′-oxy-*β*-phenyltetrahydrofurfurane; and (4) that the substance, to which Jena and Limpricht[8] assigned the formula, $C_{28}H_{24}O$, is the dimolecular anhydride of isohydrobenzoin in an impure form. This substance was prepared by distilling the so-called isodesoxybenzoin pinacone with dilute sulphuric acid. Breuer and Zincke[9] have shown that isohydrobenzoin, by distillation with dilute sulphuric acid (20 per cent.), is converted into its dimolecular anhydride, which melts, when pure, at 102°.5.

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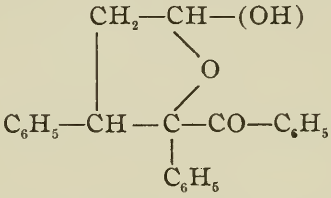
[1] Ber. d. chem. Ges., **26**, 2415.

[2] *Ibid.*, **19**, 1867.

[3] *Ibid.*, **24**, 1778.

[4] Ann. Chem. (Liebig), **155**, 96.

Study of the Tetrahydrofurfurane Derivative.



The tetrahydrofurfurane derivative is prepared and separated as described above. It melts, when recrystallized from either alcohol, benzene, or acetic acid, at 195°. On analysis and molecular weight determination, figures were obtained agreeing with the formula, $C_{23}H_{20}O_3$.

I. 0.1976 gram gave 0.5839 gram CO_2 and 0.1126 gram H_2O.

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[1] Ber. d. chem. Ges., **24**, 1778.

[2] *Ibid.*, **26**, 2413.

[3] Ann. Chem. (Liebig), **155**, 98.

[4] *Ibid.*, **155**, 79.

[5] Ber. d. chem. Ges., **4**, 336.

[6] Ann. Chem. (Liebig), **155**, 92.

[7] Ber. d. chem. Ges., **18**, 175.

[8] Ann. Chem. (Liebig), **155**, 99.

[9] *Ibid.*, **198**, 182.

II. 0.2072 gram gave 0.6122 gram CO_2 and 0.1162 gram H_2O.

III. 0.1400 gram gave 0.4115 gram CO_2 and 0.0756 gram H_2O.

	Calculated for $C_{23}H_{20}O_3$.	Found.		
		I.	II.	III.
C	80.23	80.60	80.58	80.18
H	5.81	6.30	6.23	6.00

Molecular weight determination, by the boiling-point method, with benzene as solvent, was as follows :

0.1082 gram gave an elevation of 0°.036 in 23.1 grams of the solvent.

Calculated for $C_{23}H_{20}O_3$.	Found.
344	347

The substance is insoluble in aqueous solutions of sodium carbonate, sodium hydroxide, potassium hydroxide, and barium hydroxide, but is soluble in alcoholic solutions of these substances, and may be reprecipitated by the addition of acid. It is insoluble in hot ligroin (b. p. 40° to 60°), soluble in hot benzene, alcohol, ether, acetic acid, and chloroform. With concentrated sulphuric acid it gives a deep yellow coloration, which changes to dark-red on warming. Dilute alcoholic solutions of the substance produce a deep red coloration with ferric chloride.

Phenylhydrazine, hydroxylamine, and bromine in chloroform solution do not interact with it. Chromic acid oxidizes it to benzoic acid and carbon dioxide. In the presence of air, ethyl alcohol, saturated with hydrogen chloride gas, converts it partially into cinnamic ethyl ester and benzil.

Oxidation of the Tetrahydrofurfurane Derivative.

If reference be made to the method of preparation of this derivative, it will be noted that, after the removal of alcohol, hydrobenzoin, etc., an alkaline filtrate is left from which the derivative can be obtained by acidification. If this alkaline filtrate is treated in the cold with the calculated amount of potassium permanganate, the latter is instantly reduced.

On examination of the products, it was found that instead of the tetrahydrofurfurane derivative, β-phenyl-γ-phenyl-γ-benzoylbutyrolactone had been formed. The butyrolactone derivative was separated from the reaction mixture by the same processes which were used in the isolation of the tetrahydrofurfurane derivative. It was recrystallized from ethyl alcohol, and when pure melted at 138°.5. On analysis, the following results were obtained :

I. 0.2951 gram substance gave 0.8692 gram CO_2 and 0.1451 gram H_2O.

II. 0.1924 gram substance gave 0.5650 gram CO_2 and 0.0922 gram H_2O.

	Calculated for $C_{23}H_{18}O_3$.	Found. I.	II.
C	80.70	80.33	80.09
H	5.27	5.46	5.32

This substance is soluble in hot alcohol, acetic ether, benzene, and chloroform, and almost insoluble in hot ligroin (b. p. 40° to 60°). No interaction takes place between it and phenylhydrazine, hydroxylamine, acetyl chloride, acetic anhydride, bromine, or alcoholic ammonia (in sealed tubes at 200°).

The tetrahydrofurfurane derivative, when warmed on the water-bath with nitric acid (sp. gr. 1.33), is oxidized to the butyrolactone derivative.

Acetate of the Tetrahydrofurfurane Derivative.

If the tetrahydrofurfurane derivative is boiled with a mixture of acetic anhydride and fused sodium acetate, a solution is obtained which, on being poured into a large excess of water, produces a white solid; this, upon repeated recrystallization from hot alcohol, forms large transparent plates, melting at 145°. After careful drying at 100°, figures were obtained showing it to be the monoacetyl derivative.

0.1945 gram substance gave 0.5516 gram CO_2 and 0.1033 gram H_2O.

	Calculated for $C_{25}H_{22}O_4$.	Found.
C	77.71	77.34
H	5.69	5.90

It is soluble in cold benzene, ether, acetic ether, hot alcohol, and acetic acid; insoluble in ligroin (b. p. 40° to 60°). By saponification with alcoholic potassium hydroxide it is converted into the tetrahydrofurfurane derivative. With concentrated sulphuric acid it gives a deep red coloration.

By fusion with solid potassium hydroxide, the tetrahydrofurfurane derivative is converted into benzoic acid, cinnamic acid, and some acetic acid. The fusion is best carried out as follows: Three grams of finely powdered substance are gradually added to a fused mass of 30 grams of potassium hydroxide at 200°, and the mixture thoroughly stirred. After maintaining this temperature for ten minutes the mass becomes yellow, and the odor of benzoic acid is detectable. The substance is allowed to cool, dissolved in water, and any unchanged tetrahydrofurfurane derivative filtered off. The filtrate is acidified with dilute hydrochloric acid and extracted with ether. The residue, after the removal of the ether, was found to contain the acids mentioned above. Benzoic acid was separated from cinnamic acid by sublimation, as well as by fractional recrystallization from hot ligroin (b. p. 40° to 60°). The acids were identified by their ethyl esters, solubilities, and melting-points.

Constitution of the Tetrahydrofurfurane Derivative.

The formation of a monoacetyl derivative, the partial decomposition into cinnamic ethyl ester and benzil, the oxidation to benzoic acid and carbon dioxide with chromic acid, the oxidation to the butyrolactone derivative with potassium permanganate or nitric acid, and the decomposition into benzoic acid, cinnamic acid, and acetic acid by fusion with potassium hydroxide, all accord with the view of its constitution advanced above; but this receives its greatest support from the fact that the tetrahydrofurfurane derivative may be readily prepared by the direct addition of benzoin to cinnamic aldehyde, under the influence of dilute, absolute ethyl alcoholic solution of sodium ethylate.

The conditions under which the tetrahydrofurfurane derivative was prepared were as follows: One molecule of pure benzoin (6.4 grams) and 1 molecule of cinnamic aldehyde (4 grams) were dissolved in absolute ethyl alcohol (150 cc.), and to the mixed liquids a solution (0.5 gram sodium in 30 cc. alcohol) of sodium ethylate (2 cc.) was added. The mixture assumed a deep wine color. After standing at the ordinary temperature for several hours, beautiful white crystals separated, which, on recrystallization from hot alcohol, melted at 195°. Enough water was added to the mother-liquor to produce a cloudiness, and in the course of an hour rosettes of needles separated. These were recrystallized from alcohol and melted at 160° to 161°. (The study of this latter substance is postponed.)

The analyses and molecular weight determination of the substance, melting at 195°, showed it to be $C_{23}H_{20}O_3$.

I. 0.2220 gram gave 0.6522 gram CO_2 and 0.1227 gram H_2O.

II. 0.1838 gram gave 0.5430 gram CO_2 and 0.1227 gram H_2O.

III. 0.2367 gram gave 0.6949 gram CO_2 and 0.1343 gram H_2O.

	Calculated for $C_{23}H_{20}O_3$.	Found. I.	II.	III.
C	80.23	80.12	80.56	79.76
H	5.81	6.14	5.82	6.28

The molecular weight determination by the boiling-point method, using benzene as the solvent, resulted as follows:

0.1249 gram gave an elevation of 0.035° in 27.66 grams of the solvent.

Calculated for $C_{23}H_{20}O_3$.	Found.
344	346

This substance may be mixed in any proportions with the compound obtained from benzoin and sodium ethylate alone, without change in the melting-point of either specimen. The solubilities of the two substances are the same, and both show identical chemical properties. With phenylhydrazine, hydroxylamine, etc., there is no interaction.

One molecule of the substance was dissolved in glacial acetic acid, and 5 molecules of acetyl chloride gradually added to the boiling solution, using a reflux condenser. The boiling was continued for an hour, the mixture cooled, and water added until a cloudiness appeared. In a short time large glittering crystals separated, which, after recrystallization from hot alcohol, melted at 145°. The analysis showed it to be the mono-acetyl derivative.

0.2618 gram gave 0.7467 gram CO_2 and 0.1366 gram H_2O.

	Calculated for $C_{25}H_{22}O_4$.	Found.
C	77.71	77.40
H	5.69	5.79

By saponification with alcoholic potash the acetyl derivative was reconverted into the original substance. The compound may be mixed in any proportion with the acetate of the tetrahydrofurfurane derivative without change in the melting-point.

It has been shown by Professor Alexander Smith,[1] and by the author,[2] that benzoin adds itself to benzylidene acetone or its homologues to form 1,5-diketones, which, by loss of water and ring formation, are converted into Δ_2-keto-R-hexene derivatives. Analogy leads me to assign to the substance resulting from the addition of benzoin to cinnamic aldehyde the constitutional formula given above.

The formation of the tetrahydrofurfurane derivative as one of the products of the interaction of benzoin and sodium ethylate can be explained by the assumption that there has been formed, intermediately, cinnamic aldehyde, or a mixture of benzaldehyde and acetaldehyde; benzoin then reacts, under the influence of sodium ethylate, to produce the tetrahydrofurfurane derivative. Peine[3] and Claisen[4] have shown that cinnamic aldehyde results from the interaction of benzaldehyde and acetaldehyde in the presence of sodium hydroxide or sodium ethylate. As will be shown later benzoin reacts incompletely with sodium ethylate to produce benzaldehyde.

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[1] Ber. d. chem. Ges., **26**, 65.

[2] This JOURNAL, **31**, 143.

[3] Ber. d. chem. Ges., **17**, 2117.

[4] *Ibid.*, **20**, 657.

Magnus-Lahens,[1] Marchand and Ménard,[2] and Krämer and Pinner[3] have shown that ethyl alcohol, under various conditions, in the presence of air, is partially converted into acetaldehyde.

The study of similar reactions as applied to other ketols will be continued in this laboratory.

In conclusion, I wish to express my most sincere thanks to Professor Alexander Smith for the many favors which he has shown me during the work of the present paper.

PECK CHEMICAL LABORATORY,
WABASH COLLEGE,
CRAWFORDSVILLE, IND.

Preliminary Contribution from the Chemical Laboratory of Johns Hopkins University.

ON THE ACETYL DERIVATIVES OF PHENYLURAZOLE.

BY S. F. ACREE.

At the beginning of this investigation only three acetyl derivatives of phenylurazole had been made; namely, phenylacetylurazole, m. p. 175°, phenyldiacetylurazole, m. p. 165°, and 1-phenyl-4-methylacetylurazole, m. p. 113° to 115°. As nothing definite was known in regard to the position of the acetyl groups in these compounds, the first problem that presented itself was the determination of the position of the acetyl group and of the hydrogen atom belonging to the urazole ring in phenylacetylurazole.

There are ten[4] possible tautomeric formulas for this phenylacetylurazole, and four possible positions for the acetyl group.

It had been found that diazomethane[5] reacts very readily with the urazoles even at —20°, whereby methyl derivatives are formed. It was, therefore, hoped that the action of diazomethane on Pinner's phenylacetylurazole, and on others that I might make, could be carried out under conditions which would prevent the rearrangement of the phenylacetylurazole or of the methylated products. The determination of the constitution of the phenylmethylacetylurazole would probably simultaneously give the constitution of the phenylacetylurazole.

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[1] J. prakt. Chem., **65**, 313.

[2] *Ibid.*, **65**, 138.

[3] Ber. d. chem. Ges., **2**, 401.

[4] Acree: This JOURNAL, **27**, 118; Ber d. chem. Ges., **35**, 553. An example of tautomerism in the urazole series recently discovered by Busch (Busch and Opfermann: Ber. d. chem. Ges., **37**, 2333) now makes it necessary to recognize the possibility of a larger number of these tautomeric forms.

[5] Acree: Ber. d. chem. Ges., **36**, 3139.

Accordingly, a sample of phenylacetylurazole was made by Mr. F. B. Laist, following Cuneo's directions.[1] It melted at 173°, and analysis and titrations showed it to be pure. When the substance was treated with diazomethane, under definite conditions, there was obtained 1-phenyl-4-methylacetylurazole,[2] which melted at 94°. I repeated Mr. Laist's experiments and obtained the same substance melting at 94°. When this was melted and allowed to solidify, or was heated to 140° and allowed to solidify, it subsequently melted at 113° to 115°. The same rearrangement was found to have taken place spontaneously when the original substance was examined a few months after its preparation. The rearranged product, melting at 113° to 115°, was found to be identical with Busch's 1-phenyl-4-methylacetylurazole,[3] m. p. 113° to 115°, which was made by the action of acetic anhydride and sodium acetate on 1-phenyl-4-methylurazole. The substances had the same solubilities and crystalline form, and a mixture of the two preparations melted at 113° to 115°. Apparently, then, I had here two different 1-phenyl-4-methylacetylurazoles. Provided they are not physical isomers, the one melting at 94° would probably best be represented by Formula III., and that melting at 113° to 115° by Formula IV.

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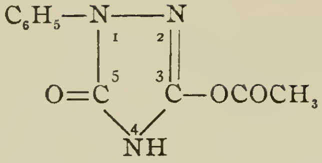
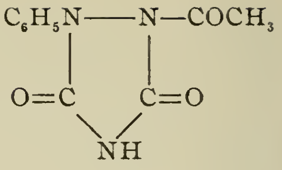
[1] Centrbl., 1, 38 (1898).

[2] Acree: Ber. d. chem. Ges., **36**, 3143.

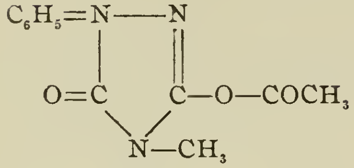
[3] *Ibid.*, **34**, 2333 (1901). In Professor Busch's article this substance was described as having the melting-point 129°. At my request, Professor Busch determined the melting-point of a sample of this substance still on hand and found it to be 113° to 115°. The mistake in the melting-point is therefore due to a clerical error. I take this occasion to thank my colleague for kindnesses shown me on many occasions.



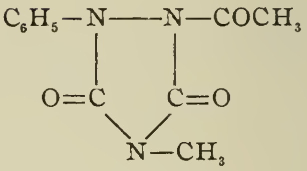
I.



II.



III.



IV.

As it was desired to subject these two substances to further chemical reactions to determine the correctness of these formulas, some months later, in the University of Berlin, I attempted to prepare a large quantity of the substance melting at 94°. The former experiments were repeated several times, apparently under the conditions that had previously been successful, but in every case only the substance melting at 113° to 115° was obtained. Other experiments, in which the temperature and pressure were varied widely, also gave the higher melting isomer. Then it was discovered that the same sample of phenylacetylurazole, which, when treated with diazomethane a few months before, had yielded the lower melting isomer, now gave the higher melting compound under the same conditions. Briefly, a certain sample of phenylacetylurazole, m. p. 173°, gave with diazomethane 1-phenyl-4-methylacetylurazole, m. p. 94°, which easily rearranged into another 1-phenyl-4-methylacetylurazole, melting at 113° to 115°. A few months later the same sample of phenylacetylurazole, still melting at 173°, gave, with diazomethane, directly the 113° to 115° isomer. Provided physical isomerism is excluded, which must be established by subjecting the substances to further chemical reactions, the first sample of phenylacetylurazole probably had the labile formula (I.) and rearranged (at least partly) into the stable substance with Formula II.

Several samples of this phenylacetylurazole, melting at 175°, were made by the action of acetyl chloride or acetic anhydride on phenylurazole, and on silver phenylurazole. When treated with diazomethane these all gave the isomer melting at 113° to 115°. 1-Phenyl-4-methylurazole, or its silver salt, treated with acetyl chloride or acetic anhydride, yields only the isomer melting at 113° to 115°. Although in many experiments the temperature was kept at —20°, the labile form' melting at 94°, was never again obtained.

Qualitative experiments on the 94° melting-point isomer, and on the one melting at 113° to 115°, showed that the labile form is more readily hydrolyzed by alkalies. I suspect that, in some of these products, I have mixtures of the labile and the stable forms, melting at the point of fusion of the stable form, and I am now investigating this further.

It is highly probable that phenylacetylurazole, prepared according to Cuneo, consists generally of a mixture of two substances, represented by Formulas I. and II. ; the first formula represents the labile form, and the second one the stable substance.

The normal reaction product of acetyl chloride on mono-silver phenylurazole should be phenylacetylurazole. I always find this to be the chief product of the reaction, a small amount of phenyldiacetylurazole, melting-point 165°, occurring as a secondary reaction product.[1] The phenylacetylurazole obtained in my first experiment was impure.[2]

Wheeler and Johnson[3] describe the sole reaction product as a labile phenyldiacetylurazole, no phenyl acetylurazole being obtained by them. I have never observed the formation of this labile phenyldiacetylurazole, but this may be due to the fact that the conditions under which my experiments were performed were not the same as in those of Wheeler and Johnson.

Similarly, Wheeler and Johnson state that, by the action of ethyl iodide on mono-silver phenylurazole, they were able to obtain 1-phenyl-3,5-diethoxyurazole and phenylurazole, but no 1-phenyl-3-ethoxyurazole. This 1-phenyl-3-ethoxyurazole should be the normal reaction product, and is the chief one[1]; small amounts of 1-phenyl-3,5-diethoxyurazole and phenylurazole occur as secondary reaction products.

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[1] Acree : Ber. d. chem. Ges., **36**, 3143 ; This Journal, **31**, 188.

[2] Acree : This Journal, **27**, 132 ; Ber. d. chem. Ges., **35**, 560.

[3] This Journal, **30**, 24.

I have made it clear[2] why Wheeler and Johnson failed to obtain the 1-phenyl-3-ethoxyurazole formed in this reaction. They extracted an ethereal solution containing 1-phenyl-3,5-diethoxyurazole (insoluble in alkalies) and 1-phenyl-3-ethoxyurazole (soluble in alkalies), with an alkaline solution, thereby removing the 1-phenyl-3-ethoxyurazole from the ether solution. They then examined the latter and found the 1-phenyl-3,5-diethoxyurazole. They forgot to examine the alkaline solution, and consequently failed to find the 1-phenyl-3-ethoxyurazole.

The following experiment is a repetition of Wheeler and Johnson's work. Pure mono-silver phenylurazole (2.5 grams) was suspended in 30 cc. ether and 2.0 grams of ethyl iodide, and the mixture shaken at intervals during four days. The ether solution was then filtered, and the residue of silver iodide extracted twice with ether. The filtered ether solutions were combined and shaken well with 25 cc. normal potassium hydroxide solution, in a separatory funnel. The alkaline solution was separated from the ether, and acidified; a precipitate was obtained, which, when crystallized from 50 per cent. alcohol, weighed 0.80 gram, melted at 152°, and showed the characteristic properties of 1-phenyl-3-ethoxyurazole. The ether solution was evaporated and a residue was obtained which soon solidified; it weighed 0.35 gram and was identical with 1-phenyl-3,5-diethoxyurazole. In this experiment, then, I obtained 0.80 gram 1-phenyl-3-ethoxyurazole and 0.35 gram 1-phenyl-3,5-diethoxyurazole.

I have pointed out twice[3] before that the 1-phenyl-3-ethoxyurazole first[4] obtained by this reaction was slightly impure (melting-point 141° instead of 152°) and was incorrectly described as insoluble in alkalies. The pure substance has been proved to have the constitution assigned to it, and to be identical with the phenylethoxyurazole made by Wheeler.[1]

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[1] Ber. d. chem. Ges., **36**, 3147.

[2] This JOURNAL, **31**, 186.

[3] Ber. d. chem. Ges., **36**, 3140, 3146; This JOURNAL, **31**, 185.

[4] This JOURNAL, **27**, 131; Ber. d. chem. Ges., **35**, 559.

Part of this work was done at the University of Utah.

CHICAGO, July 27, 1904.

OBITUARY.

CLEMENS WINKLER.

The death of Clemens Winkler took place October 8, at Dresden. He was born December 26, 1838, in Freiberg, Saxony, where he spent practically his whole life ; he was a student, and subsequently, in 1873, became Professor of Chemistry, in the "Bergakademie," there. His Ph.D. was obtained from Leipzig. Winkler's discovery of germanium, in 1886, was of unusual interest because the existence of this element, under the name of ekasilicon, had been foretold by Mendeléeff fifteen years previously.

The contact process for the production of sulphur trioxide, and therefore of fuming sulphuric acid, although originated by Winkler, became a technical success only in consequence of the more recent work of chemists attached to the Badische Anilin-Soda Fabrik. Winkler's specialty was analysis ; he worked out a number of volumetric and gravimetric methods of various kinds, but his name, in this department of chemistry, is most familiar in connection with technical gas analysis. By his novel apparatus and through his books on the subject, which appeared in 1876 and 1885, as well as by his teaching, he effected something like a revolution in certain industrial processes, and enabled them to be placed on a scientific basis. On account of ill-health his teaching activities have been much restricted since 1892.

REVIEWS.

THE ELEMENTS OF CHEMISTRY. BY M. M. PATTISON-MUIR, M.A., Fellow and Praelector in Chemistry, of Gonville and Caius College, Cambridge. London : J. and A. Churchill. 1904. pp. 554.

Here is another effort to present the elements of chemistry in a scientific way. The author says : "The objects of this book are: To present some of the fundamental facts, generalizations, principles, and theories of chemistry, lucidly, methodically, and suggestively ; to train the student in a few of the methods of investigation and reasoning which have been used in the past, and some of the methods which are used today, for discovering and co-ordinating the connections between the properties and the compositions of systems of homogeneous substances; to attempt to lay the foundations of chemistry in such a way that the student may be prepared to go more deeply into the science if he wishes so to do.

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[1] J. Am. Chem. Soc., 1900, p. 377.

"I have avoided minute details of special facts which have not a direct bearing on the general development of the science. Of course, I have omitted vast quantities of chemical facts of great importance.

"I hope I have not merely added one more illustrated catalogue of chemical odds and ends to the many which have already appeared under the title of "A Text-book of Chemistry.""

The book contains twenty-six chapters and an appendix, the titles of which are: I. Some of the marks of those changes, the elucidation whereof is the subject of chemistry. II. The study of composition; the laws of chemical combination. III. The determination of the combining weights of elements, and the reacting weights of compounds; chemical symbols and formulae. IV. Introduction to the study of interactions and the connections between them and composition; acids; basic and acidic oxides; metallic and non-metallic elements. V. Chemical nomenclature. VI. Oxygen and hydrogen. VII. Compounds formed by the union of hydrogen and oxygen; water and hydrogen peroxide. VIII. Nitrogen and some of its compounds. IX. Sulphur and some of its compounds. X. Potassium and sodium and some of their compounds. XI. Iron and a few of its compounds. XII. The chemical character of metals and non-metals illustrated by certain compounds of manganese and some compounds of chromium. XIII. Chemical characters of elements illustrated by oxides of antimony, arsenic, bismuth, and tin. XIV. Chlorine, bromine, fluorine, and iodine, and some of their compounds. XV. Oxidation and reduction; oxidizers and reducers. XVI. The molecular and atomic theory. XVII. Some applications of the molecular and atomic theory, chiefly to classes of facts already considered. XVIII. Isomerism and structural formulae. XIX. The periodic law. XX. The measurement of the thermal values of chemical changes. XXI. Phosphorus; its oxides, hydrides, and some of its acids. XXII. Carbon and silicon and a few of their compounds. XXIII. Magnesium, zinc, cadmium, and mercury; calcium, strontium, and barium. XXIV. Some of the physical and chemical properties of copper, lead, and aluminium. XXV. A few physical and chemical properties of palladium and platinum. XXVI. Argon and its companions; concluding remarks. Appendix. Short descriptions of the general chemical characters of each of the eight groups of elements.

This will give some idea of the method of treatment adopted by the author. In brief it may be characterized as emphasizing the laws and theories rather than the facts upon which these laws and theories are based. To be sure, the facts are not ignored, but the student of the book would be likely to get the impression that they are of secondary importance and of interest only in so far as they furnish a scaffolding for the building up of generalizations and theories. This is by no means the first attempt that has been made to bring out the essence of chemistry. Like the others, it is not wholly successful as the author would, no doubt, be the first to admit. But it will be helpful to teachers in many ways and they are advised to study it.

Mr. Muir has always been interested in the physical side of chemical phenomena and we therefore naturally turn to those parts of the book that deal with the ionic theory, the law of mass action, and related concepts, without which, in these latter days, even an elementary (even the most elementary) textbook of chemistry is not regarded as complete by the regenerate. The ionic hypothesis, of course, receives its full due. Ions are first mentioned on page 199, under "electrolysis of dilute sulphuric acid." They are introduced by the statement: "The minute particles of elements, or groups of elements, which are supposed to carry electric charges are called ions." Then, beginning on page 224, about seven and a half pages are given to "the ionic hypothesis of the strengths of acids and bases." That the author is not dogmatic is shown by this passage, which is fairly typical: "All acids, bases, and salts, and generally, all compounds which conduct the electric current, are supposed to be separated into ions more or less completely, when they are dissolved in much water, and in certain other solvents; and the electric conductivities of these solutions are regarded as dependent on the number of ions which they contain. The electric current is not supposed to decompose the electrolyte into its ions, but merely to direct the ions, the anions towards the anode the kations towards the kathode. Again: "The ionic hypothesis bids us think of dilute solutions of hydrochloric, sulphuric, nitric, and acetic acids as containing ions of $H^{\cdot}$ and Cl', $H^{\cdot}H^{\cdot}$ and SO_4'', $H^{\cdot}$ and NO_3', $H^{\cdot}$ and $C_2H_3O_2'$ (besides particles of HCl, H_2SO_4, HNO_3, and $H.C_2H_3O_2$)."

The law of mass action appears first in rudimentary form, on page 129, where the action of steam upon iron is discussed, then more fully (page 217), under the head of "Equilibrium of Systems in Solution." Whether the student will profit by these paragraphs will depend upon his age, intellectual power, and experience. The phase rule—the phase rule, I say,—is not mentioned in the book! Personally, I have no objection to this omission from an elementary book, but there are those to whom it will give acute pain. The question that constantly presents itself to the teacher of chemistry is, what is likely to do the students the most good? Suppose a student is to spend one year studying chemistry in high school or college, what is the best thing to do for him? Is it best to make him learn a lot of phrases that can have little or no meaning for him, or to let him become acquainted with a certain number of clearly defined chemical phenomena by personal contact? Of course, many will answer, let us have the advantage of both methods. I am coming more and more to think that the first year should be given largely to the study of phenomena in the laboratory. If the student goes on for a second year, he will be in a position to appreciate and understand the generalizations and theories. If he doesn't go on, he loses nothing by not studying these generalizations and theories in the first year, for he cannot grasp them in that stage of his work.

It is to be hoped that teachers of chemistry will study Mr. Muir's book. Perhaps some of them may be led to try it with their classes. I. R.

FOOD INSPECTION AND ANALYSIS. By ALBERT E. LEACH, S.B., Analyst of the Massachusetts State Board of Health. First edition; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 787.

This volume of 787 pages and 40 plates of photo-micrographs is a timely contribution to the literature of food inspection and analysis.

The rapid increase in the number of national and state laws relative to the inspection of food has rendered necessary the creating of a special branch of chemistry devoted to this purpose. By far the greater amount of work of food inspection is of a chemical character, including the application of the microscope for chemical purposes. There are now many chemists in this country directly connected with national, state, and municipal food control, and a great many more are called upon to do work for food manufacturers and dealers. To all of these, as well as to the general chemist, this book will prove a great aid. In addition to the purely chemical part of the work, much attention is given to a discussion of the nature and extent of food adulteration, and also to the methods of conducting inspections, other than the purely chemical examination. Some attention is also paid to the general composition of food.

It is believed that the part of the book relative to microchemistry is the most useful contribution of the kind which has been made in the domain of food inspection.

The work is divided into nineteen chapters, dealing with: Food Analysis and State Control, 1–11; The Laboratory and Its Equipment, 12–34; Food, Its Functions, Proximate Components and Nutritive Value, 35–46; General Analytical Methods, 47–69; The Microscope in Food Analysis, 69–87; Milk and Milk Products, 88–164; Flesh Foods, 165–202; Eggs, 203–211; Cereals and Their Products, Legumes, Vegetables, and Fruits, 212–275; Tea, Coffee and Cocoa, 276–309; Spices, 310–368; Edible Oils and Fats, 368–460; Sugar and Saccharin Products, 461–522; Alcoholic Beverages, 523–607; Vinegar, 609–627; Artificial Food Colors, 661–681; Artificial Sweeteners, 682–688; Canned and Bottled Vegetables, Relishes and Fruit Products, 689–756. The Appendix gives an account of the Zeiss Immersion Refractometer and other apparatus used in food analysis. The photo-micrographs represent the cereals, legumes, miscellaneous starches, coffee, spices, spice adulterants, and edible fats.

The book is well printed on good paper and well bound, though a trifle heavy for use. The index, a matter very often neglected by authors, is very satisfactory, covering 16 pages.

Legumes, perhaps, might be classed as vegetables or as a sub-class under vegetables.

Specific reference can be made to only a few parts of the work. In regard to antiseptics in food, the author calls attention to the chaotic condition of food laws relative to chemical preservatives. In some localities certain antiseptics are specifically allowed and others are prohibited. Some of the states, as, for example, Massachusetts, have special laws under which it is required that, in the case of a food treated with antiseptics, the name and percentage of the added substance must plainly appear upon the label. Such laws as these make the chemists' task comparatively easy, or perhaps it would be better to say, the prosecutors' task. The fact that the author gives certain formulas for chemical preservatives, recommended for sausage meat, cider, beer, etc., is unfortunate, as such a recommendation will be cited as an excuse for their use. Such, of course, was not the intention of the author, but the user of food preservatives, seeking for justification, will not bother himself about the author's intention.

In the titration of boric acid the author mentions only the use of glycerol, although it has been found by experiments that the Jones method, which consists of substituting mannitol for glycerol, gives a more satisfactory result. A comparison of the glycerol and mannitol methods in the Bureau of Chemistry has shown the superiority of the latter.

The subject of artificial sweeteners is thoroughly treated by the author and is one of distinct importance at the present time. The use of saccharin (the name itself is highly objectionable) in food products is becoming quite general in this country, although it is forbidden in many European countries. The consumer of a product to which saccharin has been added believes that the sweet taste is due to sugar and thus is the victim of deception. Those who use saccharin think it has no antiseptic properties, but many authors claim that it is in itself antiseptic. It is evident that the use of all artificial sweeteners, except cane-sugar, should be noted on the label of food products.

The chapter on alcoholic beverages is notably interesting. I must object, however, to the definition of wine, which is as follows: "Wine in its broadest sense is the fermented expressed juice of any fruit." This statement is, I think, erroneous. The term "wine," for common and technical purposes, should be reserved only to apply to the pure fermented juice of the grape. If other fruits are used in the making of it, they should be named in conjunction with the term as, for instance, blackberry wine.

The author has fallen into a common error in assigning a misleading meaning to the word "Champagne." He gives it as a generic term for sparkling wine, when, in point of fact, the term should be applied only to the sparkling wine made in Champagne. Likewise the terms "Madeira" and "Sherry" should only be applied to wines of that character made in Madeira, or in or near Xeres de la Frontera, Spain, and the term "Port" should only be applied to wine made in or near Oporto.

A statement in regard to sugaring wine appears on page 561, *viz.*: "The European wine-raising countries are not disposed to regard the reinforcement of wine by added cane-sugar in the must as in itself a fraud, unless water is also added or unless some other form of adulteration is practiced at the same time." This statement needs a word of explanation. In France the addition of sugar to the marc or pomace of wine is absolutely prohibited except in the manufacture of wine for domestic use, and the amount of sugar which is permitted for this purpose is limited strictly to 50 kilos for each member of the family. A sugar-wine is in no case allowed to enter commerce. The best wine-growers deplore the use of sugar in the manufacture of wine and are making determined efforts to prevent it.

In Germany the addition of sugar solutions to wine is permitted, provided the quantity added is not sufficient to reduce the natural extract of the wine below that of normal pure wine. The expensive types of genuine wine, however, do not have any added sugar.

In the definition of whiskey the author also includes the potato as one of the sources from which whiskey is made. I consider it unfortunate to thus extend the definition of whiskey. A better definition, it seems to me, is the liquor resulting from the distillation of the fermented mash of cereal grains, the starch of which has been converted into sugar by malt. Potable whiskey is whiskey stored in wood a sufficient length of time to reduce the percentage of fusel oil to less than 0.25. The burnt taste of whiskey, due to creosote, mentioned on page 597, is characteristic of Scotch rather than Irish whiskey, as stated. Particular attention is called to these definitions by reason of the fact that the Congress of the United States has authorized the Secretary of Agriculture to fix standards of purity for all these bodies, and these standards have been adopted by the author in so far as they have been proclaimed. It is evident, however, that some of the definitions used by him as, for instance, those mentioned above, will be cited hereafter in courts where they differ from those which are yet to be established.

The chemical methods described in the book are to be highly commended and, in fact, the whole book is one which has been exceedingly well done and which, despite some minor defects, such as those pointed out, will prove of immense value to the profession. H. W. WILEY.

THE VEGETABLE ALKALOIDS, WITH PARTICULAR REFERENCE TO THEIR CHEMICAL CONSTITUTION. By DR. AMÉ PICTET, Professor in the University of Geneva. From the second French edition. Rendered into English, Revised, and Enlarged, with the Author's sanction, by H. C. BIDDLE, PH.D., Instructor in the University of California. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1904. 8vo. vii + 505 pp. Cloth, $5.00.

The translator introduces this work thus : " Since the appearance, in 1897, of the second edition of Professor Amé Pictet's work, 'La Constitution Chimique des Alcaloides Végétaux,' marked advances have been made in our knowledge of the alkaloids. * * * *

"These advances have precluded a simple translation of the French edition, and have necessitated the complete rewriting of several chapters and the revision of the entire work. It is believed that the present English edition fairly sets forth the latest conceptions regarding the constitution of the more important alkaloids."

The Author says: "We shall consider that the expressions *vegetable alkaloids* and *vegetable bases* are identical in meaning and that they include all those substances which are directly obtained from the plant and which are able to unite with acids to form salts."

"The work is divided into two parts. The first part gives a rapid review of the *artificial derivatives of pyridine*. * * *

"In the second part we shall seek to gather together systematically the experimental results which have thus far been derived from the study of the chemical constitution of the natural alkaloids, and to discuss the theoretical conclusions which have been drawn from these results. No attempt will be made to present a complete monograph of the vegetable alkaloids; we shall not consider in detail either their physiological or physical properties, nor shall we present the specific tests employed in detecting the natural bases. Attention will be fixed rather on the purely chemical behavior of the alkaloids and the bearing of this on their chemical constitution."

This book is altogether the best summary of our knowledge of the important class of compounds it deals with. It is well and interestingly written and will be found most useful by chemists. It contains full references to the literature.

About twenty pages are given to the alkaloids of the hemlock; forty-five pages to the coca alkaloids; fifty pages to the opium alkaloids; nearly fifty pages to the cinchona alkaloids. The xanthine group, the asparagine group, and the chlorine group are also accorded full treatment.

The book ought to be in every chemical library. I. R.

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$C_5H_6O_2N_2S$. 2-Thio-5-methylbarbituric acid. *Wheeler* and *Jamieson*.......... 352
$C_5H_6N_3SCl$. 2-Methylmercapto-4-chlor-6-aminopyrimidine. *Wheeler* and *Jamieson*........................ 347
$C_5H_7O_2N_3S$. 2-Methylmercaptouramil. *Wheeler* and *Jamieson*................. 351

5 V.

$C_5H_4O_5NSCl$. β-Sulphamido-δchlorpyromucic acid. *Hill* and *Sylvester*....... 209
Also some salts.
$C_5H_4O_5NSBr$. β-Sulphamido-δ-brompyromucic acid. *Hill* and *Sylvester*...... 222
Also some salts.
$C_5H_5O_4N_2SCl$. β-Sulphamido-δ-chlorpyromucamide. *Hill* and *Sylvester*...... 206
$C_5H_5O_4N_2SBr$. β-Sulphamido-δ-brompyromucamide. *Hill* and *Sylvester*...... 219
$C_5H_6O_3NSBr$. β-Sulphamido-δ-methylbromfurfurane. *Hill* and *Sylvester*..... 199

C_6-GROUP.

$C_6H_3I_3$. Triiodbenzol. *Jackson* and *Langmaid*.............................. 300
$C_6H_6O_2$. Methylfurfurol. *Hill* and *Sylvester*.............................. 187
$C_6H_6O_3$. δ-Methylpyromucic acid. *Hill* and *Sylvester*...................... 187
$C_6H_8O_7$. Citric acid, hydrates of. *Jones* and *Gelman*....................... 336
$(C_6H_{10}O_5)x$. Inulin. *Dean*.. 69
$C_6H_{10}O_6$. Mannite, hydrates of. *Jones* and *Gelman*......................... 325
$C_6H_{12}O_6$. Fructose, hydrates of. *Jones* and *Gelman*........................ 323
$C_6H_{12}O_6$. Glucose, hydrates of. *Jones* and *Gelman*......................... 321
$C_6H_{12}O_6$. Glucose. *Kastle* and *McCaw*...................................... 376
$C_6H_{15}N$. Triethylamine. *Willcox*.. 461, 466

3 VI.

$C_6O_6N_3Cl_3$. Trichlortrinitrobenzol. *Jackson* and *Smith*...................... 168
$C_6H_3O_9N_3$. Trinitrophloroglucine. *Jackson* and *Smith*........................ 173
$C_6H_4OCl_2$. 2,4-Dichlorphenol. *Upson*.. 29
$C_6H_4NCl_3$. Trichloraniline. *Jackson* and *Smith*............................... 171
$C_6H_4NI_3$. Triiodaniline. *Jackson* and *Langmaid*............................... 300
C_6H_5OCl. *o*-Chlorphenol. *Upson*... 26
C_6H_5OBr. *p*-Bromphenol. *Upson*.. 27
$C_6H_6O_2N_2$. *m*-Nitraniline. *Alway* and *Pinckney*............................. 399
$C_6H_6O_2N_2$. *m*-Nitraniline. *Johnson* and *Menge*.............................. 364
$C_6H_6O_3Br_2$. Mucobromic ester. *Hill* and *Black*............................... 228
$C_6H_6O_6S$. Sulphomethylpyromucic acid. *Hill* and *Sylvester*..................... 188
C_6H_6NCl. *m*-Chloraniline. *Johnson* and *Menge*................................ 366
$C_6H_8ON_2$. 2-Oxy-4,6-dimethylpyrimidine. *Wheeler* and *Jamieson*................. 357
$C_6H_8N_4S$. 2-Methylmercapto-4,6-diaminopyrimidine. *Wheeler* and *Jamieson*.. 339
$C_6H_9O_2N_3$. 5-Dimethylaminouracil. *Wheeler* and *Jamieson*..................... 355
$C_6H_9O_2N_3$. 4-Methyl-5-methylaminouracil. *Wheeler* and *Jamieson*............... 355
$C_6H_9O_3Cl$. α-Chloracetoacetic ester. *Willcox*................................ 449, 473
$C_6H_9O_3Na$. Sodium formylethylpropionate. *Johnson* and *Clapp*.................. 136

4 VI.

$C_6HO_4N_2I_3$. 1,3,5-Triiod-2,4-dinitrobenzol. *Jackson* and *Langmaid* 300
$C_6H_2O_4N_2I_2$. Diioddinitrobenzol. *Jackson* and *Langmaid* 304
$C_6H_4O_3NCl$. 4-Chlor-2-nitrophenol. *Upson* 22, 25
$C_6H_4O_3NBr$. 4-Brom-2-nitrophenol. *Upson* 27
$C_6H_5O_4SK$. Potassium phenylsulphate. *Willcox* 459
C_6H_6ONCl. 4-Chlor-2-aminophenol. *Upson* 25
$C_6H_6O_6NK$. Potassium ethylnitromaleate. *Hill* and *Black* 232
$C_6H_6N_2SCl_2$. 2-Methylmercapto-4,6-dichlor-5-methylpyrimidine. *Wheeler* and *Jamieson* 353
$C_6H_7O_3NS$. Phenylsulphamic acid. *Willcox* 469
$C_6H_7O_5NS$. β-Sulphamido-δ-methylpyromucic acid. *Hill* and *Sylvester* 193
Also some salts.
$C_6H_7O_6NS_2$. Phenylimidosulphonic acid. *Willcox* 469
$C_6H_8O_2N_2S$. 2-Methylmercapto-4,6-dioxy-5-methylpyrimidine. *Wheeler* and *Jamieson* 353
$C_6H_8O_2N_2S$. 2-Thio-5-ethylbarbituric acid. *Wheeler* and *Jamieson* 352
$C_6H_8O_4N_2S$. β-Sulphamido-δ-methylpyromucamide. *Hill* and *Sylvester* 190
$C_6H_{15}O_3NS$. Diethylsulphamic acid, ethyl ester, or diethylaminosulphone ethyl ester. *Willcox* 462, 464, 466

5 VI.

$C_6H_4O_3NClBr$. 4-Chlor-6-brom-2-nitrophenol. *Upson* 31

C_7–GROUP.

C_7H_6O. Benzaldehyde. *Garner* 595
$C_7H_6O_2$. Benzoic acid. *Garner* 590, 594, 603
C_7H_8O. Benzyl alcohol. *Garner* 598
C_7H_9N. *p*-Toluidine. *Alway* 391
C_7H_9N. *p*-Toluidine. *Johnson* and *Menge* 367
$C_7H_{12}O_4$. Ethyl malonate, for preparation of thiobarbituric acid. *Wheeler* and *Jamieson* 345

3 VII.

$C_7H_5O_3N$. *p*-Nitrobenzaldehyde. *Alway* and *Bonner* 392
$C_7H_5O_3N$. *p*-Nitrobenzaldehyde. *Alway* and *Pinckney* 398
$C_7H_5O_3N$. *m*-Nitrosobenzoic acid. *Alway* 390
$C_7H_5O_3N$. *p*-Nitrosobenzoic acid. *Alway* 389
$C_7H_5O_4N$. *m*-Nitrobenzoic acid. *Alway* 390
$C_7H_5O_4N$. *p*-Nitrobenzoic acid. *Alway* 389
$C_7H_6OBr_2$. 2,6-Dibrom-4-cresol. *Upson* 34
$C_7H_6OBr_2$. 4,6-Dibrom-2-cresol. *Upson* 33
$C_7H_7O_2N$. Nitrotoluene. *Alway* and *Bonner* 393
$C_7H_7O_3N$. *o*-Nitro-*o*-cresol. *Upson* 21
$C_7H_7O_3N$. 2-Nitro-*m*-cresol. *Upson* 19
$C_7H_7O_3N$. *o*-Nitro-*p*-cresol. *Upson* 15
C_7H_9ON. *p*-Anisidine. *Johnson* and *Menge* 367
$C_7H_{10}N_2S$. 2-Methylmercapto-4,6-dimethylpyrimidine. *Wheeler* and *Jamieson* 356
$C_7H_{11}O_4Na$. Sodic malonic ester. *Jackson* and *Langmaid* 304

4 VII.

$C_7H_3O_6N_3Cl_2$. Dichlortrinitrotoluene. *Jackson* and *Smith* 178
$C_7H_4O_3NI_3$. Triiodnitroanisol. *Jackson* and *Langmaid* 302

$C_7H_6O_3NBr$. 4-Brom-6-nitro-2-cresol. *Upson* 33

$C_7H_{10}O_2N_2S$. 2-Methylmercapto-4,6-dioxy-5-ethylpyrimidine. *Wheeler* and *Jamieson* 353

$C_7H_{10}N_3SCl$. 2-Methylmercapto-4-chlor-5-methyl-6-methylaminopyrimidine. *Wheeler* and *Jamieson* 354

5 VII.

$C_7H_{16}O_4ClSNa$. From ethylchlorsulphonate and sodium amylate. *Willcox* 448

C_8-GROUP.

$C_8H_{10}O$. Phenetol. *Willcox* 476

$C_8H_{10}O_8$. Succinic peroxide acid. *Clover* and *Houghton* 55

$C_8H_{11}N$. Dimethylaniline. *Willcox* 450, 452

$C_8H_{11}N$. Ethylaniline. *Willcox* 469

$C_8H_{14}O_4$. Ethylmethylmalonate. *Wheeler* and *Jamieson* 352

$C_8H_{14}O_4$. Suberic acid. *Clover* and *Houghton* 66

3 VIII.

$C_8H_7O_2N$. Carbonyl-*o*-amino-*p*-cresol. *Upson* 17

$C_8H_7O_3N$. Methyl-*p*-nitrosobenzoate. *Alway* and *Gortner* 402

$C_8H_7O_5N$. *o*- and *p*-Nitrophenyl methyl carbonate. *Upson* 14

$C_8H_8O_2N_2$. Glyoxylic acid. *Hill* and *Black* 235

$C_8H_9O_3N$. *o*- and *p*-Aminophenyl methyl carbonate. *Upson* 14

$C_8H_{12}O_2N_2$. *p*-Toluene-*m*-azobenzoic acid. *Alway* 391

$C_8H_{12}NCl$. Dimethylphenylammonium chloride. *Willcox* 451

$C_8H_{14}O_2N$. Nitrosoisocampholactone. *Noyes* and *Taveau* 288

$C_8H_{20}NCl$. Tetraethylammonium chloride. *Willcox* 461

4 VIII.

$C_8H_4O_{14}N_2Ba_3$. Barium nitromalate. *Hill* and *Black* 237

C_8H_5ONS. Benzoyl rhodanide. *Johnson* and *Menge* 368

$C_8H_5ONCl_2$. Benzoylisocyanchloride. *Johnson* and *Menge* 371

C_8H_6ONCl. Ethenyl-4-chlor-2-aminophenol. *Upson* 42

$C_8H_6O_6N_3Cl$. 5-Chlor-2,4,6-trinitroxylol. *Jackson* and *Smith* 181

$C_8H_7O_3NCl_2$. 4,6-Dichlor-2-nitrophenol ethyl ether. *Upson* 29

$C_8H_8O_2NCl$. Acetyl-2-amino-4-chlorphenol. *Upson* 40

$C_8H_8O_2NCl$. 2-Amino-4-chlorphenyl acetate. *Upson* 36, 40

$C_8H_{11}O_3NS$. Dimethylaniline-*p*-sulphonic acid. *Willcox* 453, 458

$C_8H_{11}O_3NS$. Dimethylaniline sulphur trioxide. *Willcox* 450, 452, 456

$C_8H_{13}O_4NS$. Dimethylphenylammonium sulphate. *Willcox* 457

5 VIII.

$C_8H_{11}ON_2SCl$. 2-Methylmercapto-4-chlor-5-methyl-6-ethoxypyrimidine. *Wheeler* and *Jamieson* 354

$C_8H_{20}O_6N_2S_2Ba$. Barium diethylsulphamate. *Willcox* 462

C_9-GROUP.

$C_9H_6N_2$. Phenylmalonic nitrile. *Hessler* 119

C_9H_8O. Cinnamic aldehyde. *Garner* 604

$C_9H_8O_2$. Cinnamic acid. *Garner* 603

$C_9H_{12}O_8$. Succinic glutaric peroxide acid. *Clover* and *Houghton* 64

$C_9H_{12}N_2$. Acetonephenylhydrazone. *Johnson* and *Menge* 369

$C_9H_{13}N$. Pseudo-cumidine. *Johnson* and *Menge* 365

$C_9H_{14}O_2$. Isocampholactone. *Noyes* and *Taveau* 290
    Also the silver salt.

$C_9H_{16}O_4$. Ethyl ethylmalonate. *Wheeler* and *Jamieson* 352

3 IX.

$C_9H_5N_2Ag$. Silver salt of phenylmalonic nitrile. *Hessler* 125

$C_9H_5N_2Na$. Sodium salt of phenylmalonic nitrile. *Hessler* 124

$C_9H_7O_2N$. Phenylcyanacetic acid. *Hessler* 127

$C_9H_7O_3N$. *m*-Nitrosocinnamic acid. *Alway* and *Bonner* 396

$C_9H_7O_3N$. *p*-Nitrosocinnamic acid. *Alway* and *Bonner* 393

$C_9H_7O_4N$. *m*-Nitrocinnamic acid. *Alway* and *Bonner* 396

$C_9H_7O_4N$. *p*-Nitrocinnamic acid. *Alway* and *Bonner* 392

$C_9H_8ON_2$. Phenylcyanacetamide. *Hessler* 122

$C_9H_9O_3N$. Ethyl *m*-nitrosobenzoate. *Alway* and *Gortner* 401

$C_9H_9O_3N$. Ethyl *p*-nitrosobenzoate. *Alway* and *Gortner* 402

$C_9H_9O_3N$. Ethyl *p*-nitrosobenzoate. *Alway* and *Pinckney* 399

$C_9H_9O_4N$. Ethyl *m*-nitrobenzoate. *Alway* and *Gortner* 401

$C_9H_{15}ON$. Aminolauronic anhydride. *Noyes* and *Taveau* 287

4 IX.

$C_9H_7O_5NCl_2$. 4,6-Dichlor-2-nitrophenyl ethyl carbonate. *Upson* 30

$C_9H_8O_5NCl$. 4-Chlor-2-nitrophenyl ethyl carbonate. *Upson* 23

$C_9H_8O_5NCl$. 6-Chlor-2-nitrophenyl ethyl carbonate. *Upson* 26

$C_9H_8O_5NBr$. 4-Brom-2-nitrophenyl ethyl carbonate. *Upson* 28

$C_9H_9O_2NS$. Methylbenzoylthioncarbamate. *Johnson* and *Menge* 364

$C_9H_9O_3NCl_2$. 4,6-Dichlor-2-aminophenyl ethyl carbonate. *Upson* 30

$C_9H_9O_3NCl_2$. 3,5-Dichlor-6-oxyphenylurethane. *Upson* 31

$C_6H_{10}O_3NCl$. 4-Chlor-2-aminophenyl ethyl carbonate. *Upson* 23

$C_9H_{10}O_3NCl$. 6-Chlor-2-aminophenyl ethyl carbonate. *Upson* 27

$C_9H_{10}O_3NCl$. 3-Chlor-6-oxyphenylurethane. *Upson* 24

$C_9H_{10}O_3NCl$. 5-Chlor-6-oxyphenylurethane. *Upson* 27

$C_9H_{10}O_3NBr$. 4-Brom-2-aminophenyl ethyl carbonate. *Upson* 28

$C_9H_{10}O_3NBr$. 3-Brom-6-oxyphenylurethane. *Upson* 28

$C_9H_{10}O_5NI$. *Jackson* and *Langmaid* 302

$C_9H_{16}O_2NCl$. Aminolauronic acid hydrochloride. *Noyes* and *Taveau* 287

4 IX.

$C_9H_7O_5NClBr$. 4-Chlor-6-brom-2-nitrophenyl ethyl carbonate. *Upson* 31

$C_9H_9O_3NClBr$. 2-Amino-4-chlor-6-bromphenyl ethyl carbonate. *Upson* 32

$C_9H_{10}O_3NClBr$. 3-Chlor-5-brom-6-oxyphenylurethane. *Upson* 33

C_{10}-GROUP.

$C_{10}H_{14}O_8$. Glutaric peroxide acid. *Clover* and *Houghton* 65

3 X.

$C_{10}H_9O_3N$. Methyl *p*-nitrosocinnamate. *Alway* and *Bonner* 395

$C_{10}H_9O_3N$. Methyl *p*-nitrosocinnamate. *Alway* and *Gortner* 402

$C_{10}H_9O_3N_3$. Phenylacetylurazole. *Acree* 607

$C_{10}H_9O_4N$. Methyl *p*-nitrocinnamate. *Alway* and *Bonner* 395

$C_{10}H_{10}O_2N_2$. α'-Phenyl-β-ethoxyfuro-α,β'-diazole. *Johnson* and *Menge* 370

$C_{10}H_{10}O_2N_2$. α'-Ethoxy-β-phenylfuro-α,β'-diazole. *Johnson* and *Menge* 371

$C_{10}H_{11}O_2N_3$. 1-Phenyl-3-ethoxyurazole. *Acree* 610

$C_{10}H_{11}O_5N$. 2-Nitro-4-methylphenyl ethyl carbonate. *Upson* 15

$C_{10}H_{11}O_5N$. 2-Nitro-5-methylphenyl ethyl carbonate. *Upson* 20

$C_{10}H_{11}O_5N$. 2-Nitro-6-methylphenyl ethyl carbonate. *Upson* 21

$C_{10}H_{12}O_6N_2$. Dinitroresorcin diethylether. *Jackson* and *Langmaid* 303

$C_{10}H_{13}O_3N$. 2-Amino-4-methylphenyl ethyl carbonate. *Upson* 18

$C_{10}H_{13}O_3N$. 2-Amino-5-methylphenyl ethyl carbonate. *Upson* 20

$C_{10}H_{13}O_3N$. 2-Amino-6-methylphenyl ethyl carbonate. *Upson* 21

$C_{10}H_{13}O_3N$. 2-Methyl-5-oxyphenylurethane. *Upson* 22

$C_{10}H_{13}O_3N$. 3-Methyl-6-oxyphenylurethane. *Upson* 16, 19

$C_{10}H_{13}O_3N$. 4-Methyl-6-oxyphenylurethane. *Upson* 20

$C_{10}H_{16}NCl$. Dimethylethylphenyl ammonium chloride. *Willcox* 454

$C_{10}H_{17}O_3N$. Camphoramidic acid. *Noyes* and *Taveau* 287

4 X.

$C_{10}H_7O_8N_3Cl_2$. Dichlortrinitrophenylacetic ester. *Jackson* and *Smith* 175

$C_{10}H_{10}O_5NBr$. 4-Brom-2-nitro-6-methylphenyl ethyl carbonate. *Upson* 33

$C_{10}H_{10}O_5NBr$. 2-Nitro-4-methyl-6-bromphenyl ethyl carbonate. *Upson* 35

$C_{10}H_{11}O_2NS$. Benzoylimidodimethylthiocarbonate. *Johnson* and *Menge* 364

$C_{10}H_{12}O_3NBr$. 2-Amino-4-brom-6-methylphenyl ethyl carbonate. *Upson* 34

$C_{10}H_{12}O_3NBr$. 2-Amino-4-methyl-6-bromphenyl ethyl carbonate. *Upson* 35

$C_{10}H_{12}O_3NBr$. 3-Brom-5-methyl-6-oxyphenylurethane. *Upson* 34

$C_{10}H_{12}O_3NBr$. 3-Methyl-5-brom-6-oxyphenylurethane. *Upson* 36

$C_{10}H_{17}O_4NS$. Dimethylphenyl ammonium ethyl sulphate. *Willcox* 458

5 X.

$C_{10}H_{18}O_{10}NS_2K$. Potassium myronate. *Kastle* and *McCaw* 372

C$_{11}$-GROUP.

$C_{11}H_{12}O_2$. Ethyl cinnamate. *Garner* 601

3 XI.

$C_{11}H_{11}O_2N$. Phenylcyanacetic ether. *Hessler* 120

$C_{11}H_{11}O_3N$. Ethyl *m*-nitrosocinnamate. *Alway* and *Bonner* 397

$C_{11}H_{11}O_3N$. Ethyl *p*-nitrosocinnamate. *Alway* and *Gortner* 402

$C_{11}H_{11}O_3N_3$. 1-Phenyl-4-methylacetylurazole. *Acree* 607

$C_{11}H_{11}O_4N$. Ethyl *m*-nitrocinnamate. *Alway* and *Bonner* 397

$C_{11}H_{11}O_4N$. Ethyl *p*-nitrocinnamate. *Alway* and *Bonner* 394

$C_{11}H_{11}O_3N$. Ethyl *p*-nitrosocinnamate. *Alway* and *Bonner* 394

4 XI.

$C_{11}H_{10}O_2NNa$. Sodium salt of phenylcyanacetic ether. *Hessler* 122

$C_{11}H_{13}O_2NS$. Benzoylimidomethylthiolethylcarbonate. *Johnson* and *Menge* 365

$C_{11}H_{17}O_4NS$. From dimethylaniline sulphurtrioxide and acetone. *Willcox* 458

C$_{12}$-GROUP.

$C_{12}H_{22}O_{11}$. Cane sugar, hydrates of. *Jones* and *Getman* 327

$C_{12}H_{22}O_{11}$. Lactose, hydrates of. *Jones* and *Getman* 326

$C_{12}H_{22}O_{11}$. Milk sugar. *Van Slyke* and *Hart* 150

3 XII.

$C_{12}H_{11}O_4N$. 4-Oxyisoquinoline-3-carboxylic ethyl ester. *Johnson* and *Clapp* 142
$C_{12}H_{14}ON_2$. Phenylmethylcyanacetimido ethyl ester. *Hessler* 128
$C_{12}H_{14}O_6N_2$. Aniline ethyl nitromaleate. *Hill* and *Black* 233
$C_{12}H_{15}O_2N_3$. 1-Phenyl-3,5-diethoxyurazole. *Acree* 610
$C_{12}H_{15}O_9N_3$. Trinitrophloroglucine triethyl ether. *Jackson* and *Smith* 173

4 XII.

$C_{12}H_{12}O_4NNa$. Sodium salt of oxymethylenehippuric ethyl ester. *Johnson* and *Clapp* 144
$C_{12}H_{15}O_2NS$. Benzoylimidodiethylthiocarbonate. *Johnson* and *Menge* 366
$C_{12}H_{32}N_2Cl_6Pt$. Triethylamine chlorplatinate. *Willcox* 461

5 XII.

$C_{12}H_{12}O_6N_2S_2Ba$. Barium phenylsulphamate. *Willcox* 459, 469

C_{13}-GROUP.

$C_{13}H_9O_3N_3$. *m*-Nitrobenzene-*p*-azobenzaldehyde. *Alway* and *Pinckney* 398
$C_{13}H_{10}O_2N_2$. Benzene-*p*-azobenzoic acid. *Alway* 390

4 XIII.

$C_{13}H_{13}O_2N_3S$. 2-Ethylmercapto-5-benzoylamino-6-oxypyrimidine. *Johnson* and *Clapp* 144
$C_{13}H_{13}O_8N_2I$. Iodonitrophenylmalonic ester. *Jackson* and *Langmaid* 305
$C_{13}H_{15}ON_3S$. Ethylmercaptoethoxyphenyl-1,3,5-triazine. *Johnson* and *Menge*. 370
$C_{13}H_{21}O_3NS$. From dimethylaniline sulphur trioxide and trimethyl ethylene. *Willcox* 459

C_{14}-GROUP.

$C_{14}H_{10}O_2$. Benzil. *Garner* 589, 601
$C_{14}H_{12}O_2$. Benzoin. *Garner* 583
$C_{14}H_{12}O_3$. Benzilic acid. *Garner* 592, 594
$C_{14}H_{14}O_2$. Hydrobenzoin. *Garner* 592, 594
$C_{14}H_{22}O_8$. Acetylene tetracarboxylic ethyl ester. *Willcox* 474

3 XIV.

$C_{14}H_{11}O_4N_3$. Benzoylnitrophenylurea. *Johnson* and *Menge* 364
$C_{14}H_{11}N_3S$. 1,3-Diphenyl-5-mercaptotriazole. *Johnson* and *Menge* 368
$C_{14}H_{11}N_3S$. 1,5-Diphenyl-3-mercaptotriazole. *Johnson* and *Menge* 369

4 XIV.

$C_{14}H_{11}O_3N_3S$. 2-Ethylmercapto-5-phthalimido-6-oxypyrimidine. *Johnson* and *Clapp* 142
$C_{14}H_{13}O_4N_3S$. α-Phthalimido-β-pseudoethylthioureaacrylic acid. *Johnson* and *Clapp* 143
$C_{14}H_{13}ON_3S$. Benzoylphenylthiosemicarbazide. *Johnson* and *Menge* 369
$C_{14}H_{17}O_4NS$. Dimethylphenylammonium phenyl sulphate. *Willcox* 459
$C_{14}H_{18}O_3N_2S$. From dimethylaniline sulphur trioxide and aniline. *Willcox* 459

C_{15}-GROUP.

$C_{15}H_{13}O_4N_3$. Benzoylpseudomethyl-*m*-nitrophenylurea. *Johnson* and *Menge* 364

C_{16}-GROUP.

$C_{16}H_{12}N_2$. Phenylbenzylmalonic nitrile. *Hessler* 129
$C_{16}H_{16}O_2$. Ethylbenzoin. *Garner* 592
$C_{16}H_{16}O_3$. Ethylbenzilic acid. *Garner* 598

3 XVI.

$C_{16}H_{15}O_4N_3$. Benzoylpseudoethyl-*m*-nitrophenylurea. *Johnson* and *Menge* 366
$C_{16}H_{16}O_2N_2$. Benzoylpseudoethylphenylurea. *Johnson* and *Menge* 365

4 XVI.

$C_{16}H_{15}O_2N_2Cl$. Benzoylpseudoethyl-*m*-chlorphenylurea. *Johnson* and *Menge*. 366
$C_{16}H_{16}ON_2S$. Benzoylphenylthiolethylpseudothiourea. *Johnson* and *Menge* 366
$C_{16}H_{40}N_2Cl_6Pt$. Tetraethylammoniumchlorplatinate. *Willcox* 461, 466

C_{17}-GROUP.

$C_{17}H_{18}O_2N_2$. Benzoylpseudoethyl-*p*-tolylurea. *Johnson* and *Menge* 367
$C_{17}H_{18}O_3N_2$. Benzoylpseudoethyl-*p*-anisylurea. *Johnson* and *Menge* 367

4 XVII.

$C_{17}H_{17}ON_3S$. Acetone α-benzoyl-β-phenylthiosemicarbazide. *Johnson* and *Menge* 369
$C_{17}H_{18}ON_2S$. Benzoyl-*p*-tolylthiolethylpseudothiourea. *Johnson* and *Menge*. 367
$C_{17}H_{18}O_{12}N_3Cl$. Chlortrinitrophenyleneaceticmalonic ester. *Jackson* and *Smith* 179

C_{18}-GROUP.

$C_{18}H_{17}ON_2$. Phenylbenzylcyanacetic ethyl ester. *Hessler*. 130
$C_{18}H_{18}O_5N_2$. Ethyl *p*-azoxybenzoate. *Alway* and *Pinckney* 399
$C_{18}H_{20}O_2N_2$. Benzoylpseudomethylpseudocumylurea. *Johnson* and *Menge* 365
$C_{18}H_{30}O_4N_2$. Acid from action of methyl alcoholic sodium hydroxide on nitroisocampholactone. *Noyes* and *Taveau* 292

4 XVIII.

$C_{18}H_5O_{12}N_6I_7$. Addition compound of diioddinitrobenzol and triioddinitrobenzene. *Jackson* and *Langmaid* 306

C_{19}-GROUP.

$C_{19}H_{22}O_2N_2$. Benzoylpseudoethylpseudocumylurea. *Johnson* and *Menge* 368

C_{20}-GROUP.

$C_{20}H_{16}N_3$. 1,5-Diphenyl-3-phenylaminotriazole. *Johnson* and *Menge* 368

3 XX.

$C_{20}H_{15}N_4Cl$. 1,5-Diphenyl-3-*m*-chlorphenylaminotriazole. *Johnson* and *Menge* 366
$C_{20}H_{32}O_4N_2$. Condensation-product of nitrosoisocampholactone with formic aldehyde. *Noyes* and *Taveau* 291

4 XX.

$C_{20}H_{32}N_2Cl_6Pt$. Dimethylethylphenylammonium chlorplatinate. *Willcox* 454

C_{21}-GROUP.

$C_{21}H_{18}N_4$. 1,5-Diphenyl-3-*p*-tolylaminotriazole. *Johnson* and *Menge* 367

3 XXI.

$C_{21}H_{18}ON_4$. 1,5-Diphenyl-3-*p*-anisylaminotriazole. *Johnson* and *Menge* 368

C_{22}-GROUP.

$C_{22}H_{19}O_8N_5$. Dianilinotrinitrophenylacetic ester. *Jackson* and *Smith* 176

$C_{22}H_{36}O_4N_2$. Condensation-product of nitrosoisocampholactone and acetic aldehyde. *Noyes* and *Taveau* 290

C_{23}-GROUP.

$C_{23}H_{18}O_3$. β-Phenyl-γ-phenyl-γ-benzoylbutyrolactone. *Garner* 602

$C_{23}H_{20}O_3$. α'-Benzoyl-α-phenyl-α'-oxy-β-phenyltetrahydrofurfurane. *Garner* .. 600

$C_{23}H_{22}N_4$. 1,5-Diphenyl-3-pseudocumylaminotriazole. *Johnson* and *Menge* 365

C_{25}-GROUP.

$C_{25}H_{22}O_4$. Monoacetyl derivative of α-benzoyl-α-phenyl-α'-oxy-β-phenyltetrahydrofurfurane. *Garner* 602, 605

C_{34}-GROUP.

$C_{34}H_{31}O_8N_5$. Addition-compound of dianilinotrinitrophenylacetic ester. *Jackson* and *Smith* 176

C_{42}-GROUP.

$C_{42}H_{32}O_6$. Benzilbenzoin. *Garner* 597

3 XLII.

$C_{42}H_{32}O_5Na_2$. Product of the action of sodium ethylate on benzoin. *Garner*. 589, 596

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